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THE JOURNAL

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THE AMERICAN CERAMIC SOCIETY

Vol. 26 April 1, 1943 No. 4

NATURE OF GEORGIA KAOLIN: I, EVIDENCE OF CHEMICAL AND COLLOIDAL ANALYSIS*

By Lane Mitchell† and E. C. Henry

Abstract

Samples of Georgia kaolin, typical of commercial clays, were obtained at various mines operating along the Georgia Fall Line. They were tested for chemical composition, chemical stability, and colloidal behavior, and a correlation of these properties was made with the usual designations of hard, semihard, and soft. The results were consistent with the geological evidence.

I. Introduction

Confusion has been brought about in ceramic literature by the use of vague descriptive names of clays. Ceramists know from experience that one ball clay does not perform as another and that china clays cannot be substituted pound for pound for each other without regard for individual differences. Use of the name of a region to designate a clay may partly describe a type of clay, but even this procedure is not satisfactory. Some clays from the extensive producing areas of Georgia are labeled "Georgia kaolins" without further designation, but the individual variations in these clays from different mines in this wide belt are such that one clay often resembles another from a far distant source more closely than it does one nearby.

The ceramic literature contains reports of many investigators comparing Georgia kaolin with other clays, but it is practically inconceivable that these researches have involved the same or even similar clays. The result has been such a diversity of properties ascribed to Georgia kaolins that some consumers expect properties they do not find and others avoid their use because some clays may have been unsatisfactory.

Producers and some consumers have accepted the rather vague but descriptive designations of "hard," "semihard," "soft," "flint," and "bauxitic" in classifying the various Georgia kaolins. The terms, hard, semihard, and soft, refer to sedimentary kaolins having no easily recognized distinction in appearance from other china clays. Their apparent variations are principally in compaction, friability, and ease of slaking. The theories which have been advanced to account for hardness follow such characteristics as (1) fineness of particle size, (2) admixture of montmorillonite or other clay minerals with the kaolinite, and (3) presence of free silicic acid deposited with the clay. Producers reduce variations among their clays by washing and blending, but the products of different companies are not necessarily alike. The treatment given may involve the addition of various electrolytes, washing, centrifuging, filter-pressing, drying, low-temperature calcination, grinding, air separation, screening, and bleaching, depending on the requirements of the consumers. The particular method of treatment may greatly alter the properties of a clay.

Clays used in this investigation were carefully collected from operating mines along the Georgia Fall Line to prevent any alteration in the treatment by the plants. The variety of clays selected, moreover, was thought to represent typical hard, soft, and semihard types. The study was also limited to the various phenomena which might reveal the make-up of Georgia kaolins and their physical behavior under varying conditions in the clay–water system. Chemical, microscopic, thermal, and X-ray analyses and various tests of colloidal behavior were made.

II. Geological Relationships

A geological study of the clays in the different pits was made, and this study was correlated with data found in the literature.‡ Geologically, the sedimentary kaolins of Georgia usually refer to the Upper Cre-

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 21, 1942 (Materials and Equipment Division). Received May 16, 1942.

† Based on a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The Pennsylvania State College, State College, Pa., August, 1941.

‡ See p. 106, footnote 1.

TABLE I

ANALYSES OF ELECTRODIALYZED AND RAW CLAYS

Clay	Electrodialyzed*					Raw‡				
	A	B	F†	M	L	M	M nodules	M fines	Q	C§
Moisture at 100°C.	0.74	1.78	2.79	0.76	4.25	1.77	1.37	1.58	3.21	
Ignition loss	13.02	12.30	11.24	13.36	5.32	13.31	13.65	13.38	15.60	13.73
Soda	0.00	0.00	Trace	0.00	Trace	Trace	0.04	0.04	0.15	
Potash	0.00	0.00	"	0.00	"	0.2	0.15	0.16	0.66	
Lime	0.00	0.00	0.00	0.00	0.00	1.40	0.78	1.00	17.92	
Magnesia	0.12	0.48	1.24	0.30	1.39	None	None	None	2.80	
Alumina	39.68	39.18	33.84	39.36	10.82	38.90	39.65	39.85	8.76	38.85
Ferric oxide	2.65	2.96	2.55	3.53	6.03	0.58	0.33	0.59	1.22	0.21
Titania	0.51	0.53	0.78	0.62	0.22	1.20	1.02	0.90	0.66	1.44
Silica	45.00	45.74	47.31	45.02	71.63	43.50	42.54	43.32	49.34	45.37
	101.72	102.97	99.75	102.95	99.66	100.86	99.53	100.82	100.32	99.60
SiO_2:Al_2O_3	1.92	1.98	2.33	1.91	11.24	1.90	1.83	1.85	9.55	1.98
SiO_2:R_2O_3	1.83	1.89	2.26	1.84	8.31	1.88	1.82	1.83	8.73	1.98

* Analyst, J. Thomas Adair, Georgia Geological Survey, March, 1941.

† Material from clay F, deposited on negative electrode during electrodialysis, was analyzed as follows: SiO_2 31.55%, R_2O_3 (chiefly Al_2O_3) 4.80%, and undetermined 63.67%; the SiO_2 to R_2O_3 ratio was 11.30. Analyst, Robert Grace, School of Mineral Industries, Pennsylvania State College.

‡ Analyst, T. W. Kethley, Georgia Geological Survey, June, 1941.

§ From the Georgia Kaolin Co.

taceous (see Fig. 1). Most commercial deposits are in the Tuscaloosa formation. Source material for formation of the kaolins appears to have been the crystalline rocks and their weathering products, located to the north of the present Fall Line in what are now the Piedmont and Highland sections of Georgia and adjoining states.

Whether the kaolins were deposited in fresh or salt water has not been proved, but it is generally agreed that they were deposited in still offshore areas at the line of demarcation between fresh and salt water. The fineness of grain and crystalline relationships suggest that at least part of the material could have occurred in the form of aluminous or siliceous gels, precipitated by flocculation.

The sediments forming the overburden of the kaolins are evidently marine deposits. Minerals of pegmatitic origin occur in the sands and contaminate the fuller's earths and limestones. The origin of the fuller's earth is not known, but the limestone is of biochemical origin; all of the overburden of the kaolins is of Eocene age.

III. Results of Quantitative Chemical Analyses

The samples of the Georgia kaolins, together with samples of a calcareous fuller's earth (which is commercially mined in the same region) and of a concretionary clay occurring in a soft kaolin mine were analyzed. The specimens included clay A (soft kaolin), clay B (semihard kaolin), clay F (dense, concretionary clay), clay L (fuller's earth), and clay M (hard kaolin), all of which were previously electrodialyzed, dried at 60°C., pulverized, and screened through a 325-mesh sieve. Clay M, untreated, and its component parts, the clay M nodules and clay M fines, were also analyzed. Clay M nodules consisted of the nodular material left as oversize on 100- and 325-mesh screens from the wet screenings

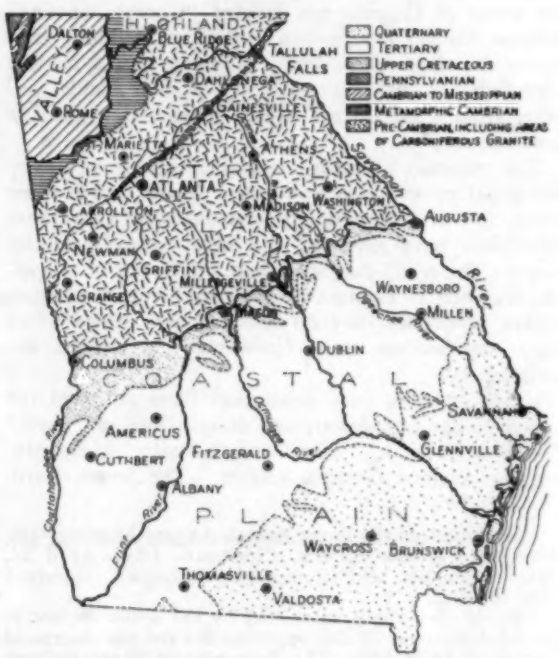

FIG. 1.—Map of Georgia showing larger geologic and topographic divisions.

[1] (*a*) C. E. Ladd, "Preliminary Report on Part of the Clays of Georgia," *Geol. Surv. Georgia Bull.*, No. 6A, pp. 81–165, 1898.

(*b*) Otto Veatch, "Second Report on Clay Deposits of Georgia," *ibid.*, No. 18, pp. 124–231, 1909.

(*c*) R. W. Smith, "Sedimentary Kaolins of Georgia," *ibid.*, No. 44, 482 pp., 1929; pp. 27–451; *Ceram. Abs.*, 8 [11] 841 (1929).

(*d*) A. C. Munyan, "Supplement to Sedimentary Kaolins of Georgia," *Geol. Surv. Georgia Bull.*, No. 44A, pp. 9–37, 1938.

(*e*) Otto Veatch and L. W. Stephenson, "Preliminary Report on Geology of the Coastal Plain of Georgia," *ibid.*, No. 26, pp. 58–306, 1911.

TABLE II
COMPARATIVE ANALYSES OF VARIOUS MATERIALS

Contents	Zettlitz kaolin*	Mo. halloysite†	Wyo. bentonite‡	Ill. illite‡	Beidellite§	Pike's Peak Ga. clay‖
Moisture at 105°C.		3.17				
Ignition loss	12.95	14.09	4.74	7.14	19.72	6.77
Soda	0.44		2.60	0.20	0.97	0.43
Potash	0.84	0.14	0.40	5.86	Trace	0.80
Lime	0.29	0.15	0.53	0.09	2.75	0.80
Magnesia	0.27	0.09	2.30	2.70	0.70	1.01
Alumina	37.40	37.99	20.80	24.99	20.27	14.34
Ferric oxide	0.65	0.51	3.05	4.68	8.68	3.90
Titania	0.18		0.15			0.72
Silica	46.90	44.10	64.60	52.79	47.28	69.62
Miscellaneous	0.167		0.46	1.10		1.68
Total	100.087	100.24	99.63	99.55	100.37	100.07

* C. S. Ross and P. F. Kerr, "The Kaolin Minerals," *U. S. Geol. Surv. Prof. Paper*, No. 165E, 29 pp. (1931); see also *Jour. Amer. Ceram. Soc.*, **13** [3] 151–60 (1930).
† Paul G. Herold, personal communication, June, 1941.
‡ R. E. Grim and W. F. Bradley, "Investigation of Effect of Heat on Clay Minerals Illite and Montmorillonite," *Jour. Amer. Ceram. Soc.*, **23** [8] 242–48 (1940).
§ F. H. Norton, "Critical Study of Differential Thermal Method for Identification of the Clay Minerals," *ibid.*, **22** [2] 54–63 (1939).
‖ H. K. Shearer, "Report on Bauxite and Fuller's Earth of the Coastal Plain of Georgia," *Geol. Surv. Georgia Bull.*, No. 31, 340 pp., 1917; see p. 174.

of a clay M slip, and the fines consisted of material recovered from the supernatant liquid after the slip had stood for several hours. Clay Q, a calcareous fuller's earth sampled from the clay which overlies the soft clay A kaolin in its pit, was analyzed in its raw condition.

The results of the analyses of the electrodialyzed and raw clays are shown in Table I. Analysis of clay C, which was obtained from the producer, is included; its previous treatment is not definitely known, although the analysis is stated to be of untreated material. For comparison, chemical analyses of various other clays are listed in Table II. These analyses were obtained from different sources, and the technique of treatment is not known.

Realizing that free silica is undoubtedly present in some of the clays and perhaps in all, the authors nevertheless calculated the SiO_2 to R_2O_3 ratios as if all silica were combined, in order to establish the probability of the presence of a substantial amount of certain minerals. Anauxite, for example, has a theoretical SiO_2 to Al_2O_3 ratio of 3, based on molecular proportions. Calculations of the molecular ratios of the selected clays give clay A a ratio of 1.92, clay B 1.98, clay F 2.33, clay M 1.91, and clay L 8.31. Anauxite, therefore, is unlikely to be present in appreciable amounts in clays A, B, and M. Although clay F has a higher silica content than the theoretical ratio for pure kaolinite, it is still low enough to be regarded as essentially kaolinite. Clay L, a fuller's earth, has sufficient silica to meet the requirements for montmorillonite and have a large excess. Gruner[2] reported 20 to 25% of cristobalite in this clay, and the chemical analysis would easily permit this amount. A considerable amount of free silica is present, which is easily visible to the naked eye and can be further substantiated under the microscope.

Clay A, a soft kaolin, shows no soda, potash, or lime, and very little magnesia. The iron oxide content falls within the limits that the kaolinite lattice may contain without distortion,[3] even without considering the possibility of free iron oxide. Electrodialysis, however, would be likely to remove free iron oxide and uncombined magnesia. If, therefore, these oxides are not within the kaolinite lattice, it would be possible for a small amount of montmorillonite to be present, although the low silica content argues against it.

Clay F shows the presence of a greater amount of magnesia than could be absorbed by the kaolinite lattice[3] if the chemical analysis is correct, and the ignition loss is slightly smaller than in the other kaolins. Some montmorillonite is possibly indicated by the analysis, assuming that all free magnesia has been removed by electrodialysis. It is interesting to note that clay F has the highest titania content of any of those analyzed, although the amount is small and the accuracy of this relationship cannot be guaranteed. A subsequent microscopic analysis showed that this clay contains less of the heavy minerals than the other clays, a fact which might lead to the premise that the titania is absorbed as a surface ion or is combined rather than trapped in the clay as an independent mineral, such as rutile, titanite, ilmenite, or leucoxene.

This premise may possibly be substantiated in part by the observation that ions are released from this clay during electrodialysis with much more difficulty than from other clays tested, as would be expected if polyvalent ions were absorbed on the surface or were built into the crystal structure. This clay, moreover, has a tan color which contrasts with the whiteness of other clays containing a larger amount of titanium.

[2] J. W. Gruner, personal communication, April 28, 1941.

[3] S. B. Hendricks and L. T. Alexander, "Minerals Present in Soil Colloids: I, Descriptions and Methods for Identification," *Soil Sci.*, **48** [3] 257–71 (1939); p. 262; *Ceram. Abs.*, **19** [7] 173 (1940).

Clay M, a hard kaolin, shows an iron content approaching the maximum amount that kaolinite can absorb. Very little montmorillonite, however, would be indicated inasmuch as the silica content is still below that theoretically required for kaolinite. Clay M nodules and clay M fines analyzed virtually the same as clay M. The only comparison between untreated and electrodialyzed clays was made on clay M. The raw clay shows essentially the same composition except that it has a higher lime and titania content and less iron than the electrodialyzed clay.

Clay L, a fuller's earth, has a high silica content and contains more iron oxide than the other clays. These observations are compatible with the idea that montmorillonite is the principal clay mineral present and that much silica is present as free quartz and cristobalite.

Clay Q, a calcareous fuller's earth that forms a part of the overburden of clay A, has a high lime content, which is observed under the microscope as calcite. The ratio of silica to alumina could satisfy the requirements for a high percentage of montmorillonite, free quartz, and cristobalite.

An analysis of clay C (another soft kaolin), supplied by the producer, shows essentially the same characteristics as clays A, B, and M. The ratio of silica to alumina is approximately equal to the theoretical requirements for kaolinite, and the clay shows less iron and more titania than other clays analyzed. The lime content of raw clays A, B, C, F, and L, which may be a factor in their hardness, was not determined.

IV. Morin Dye Tests

Tscheischwilli, Büssem, and Weyl[4] have discussed at length the use of morin dye to indicate the presence of free aluminum ions in a solution. Several drops of morin added to a solution will produce a brilliant green fluorescence under ultraviolet light if free aluminum ions are present. These ions, however, presumably are not present in nearly neutral suspensions of pure kaolinite, corundum, feldspar, and many aluminosilicates because these materials are relatively stable and insoluble. Gibbsite and bauxite, on the other hand, do release sufficient aluminum ions to cause fluorescence in the presence of morin. The appearance of a characteristic green fluorescence with morin in a slightly acid solution seems to imply the presence of active aluminum compounds.

Careful standardization of procedure permitted some quantitative estimates to be made. It was important to have the solution slightly acid because alkaline solutions produce erratic results. Strongly acid solutions, however, seemed to destroy fluorescence. Table III shows the results of these tests.

It is interesting to note that the soft kaolins, clay A and Zettlitz kaolin, showed little or no fluorescence; all hard kaolins, intense fluorescence; and fuller's earth, no fluorescence. All of the halloysites tested showed intense fluorescence as did activated alumina and aluminum nitrate.

[4] L. Tscheischwilli, W. Büssem, and W. Weyl, "Metakaolin," *Ber. Deut. Keram. Ges.*, **20** [6] 249–76 (1939); *Ceram. Abs.*, **18** [10] 279 (1939).

V. Colloidal Behavior of Georgia Kaolins

(1) Methods

The procedures described by Henry and Taylor[5] were mainly used in this investigation. Electrodialysis was carried out in Mattson-type cells. Clays were prepared for this treatment by grinding and screening through a 35-mesh screen, mixing with distilled water, and blunging into a slip in a small laboratory agitator. The resultant slip was screened through 325-mesh screens, and the tailings were saved for microscopic study. The screened slip was poured into the inner compartment of the electrodialysis cell, which was separated from the outer compartments by parchment membranes. Distilled water was used in the outer chambers. A copper negative electrode and a platinum positive electrode were connected to a 110-volt d.-c. line. The electrodialysis operation was continued in each instance until a 50-watt bulb in series did not glow appreciably after one of the periodic water changes. This was considered the end point of the operation.

There was some migration of the finest particles through the membranes. Although clays are generally considered to be negative in character, deposits were found to occur on both electrodes, a fact which suggests that some of these clays may contain positively charged components.

The electrodialyzed clays were removed from the cells, dried slowly at 60° ± 10°C., and ground to pass 35-mesh; 50-gm. portions were weighed out in a series of flasks containing 100 cc. of NaOH solution, the amount of NaOH having some definite value in the range of 0 to 100 m.e. per 100 gm. of clay. This range was considerably shortened in most instances.

A similar series of clay-electrolyte-water suspensions was prepared with each clay "as received," that is, not electrodialyzed. All of these suspensions were allowed to stand overnight and were agitated an hour in a mechanical shaker before the viscosity tests were made. A Stormer viscosimeter, which had been

[5] E. C. Henry and N. W. Taylor, "Acid and Base Binding Capacities and Viscosity Relations in Certain Whiteware Clays," *Jour. Amer. Ceram. Soc.*, **21** [5] 165–75 (1938).

TABLE III

FLUORESCENCE OF DILUTE HCl LEACHINGS OF VARIOUS MATERIALS

Material	Fluorescence
Clay A (soft kaolin)	Weak, green
Clay B (semihard kaolin)	Intense, green
Clay F (hard, concretionary clay)	" "
Clay M (hard kaolin)	" "
Clay M nodules	" "
Clay M fines	" "
Clay L (fuller's earth)	No fluorescence
Material from clay F deposited on negative electrode	Moderate, green
Activated alumina	Intense, green
Aluminum nitrate	" "
Djebel de Bar halloysite	" "
Missouri halloysite	" "
Sand from Missouri halloysite	" "
Zettlitz kaolin	No fluorescence

calibrated with oils of known viscosity, was used for the measurements. Any erratic behavior on the part of the clays, such as gelation, thixotropy, dilatency, or rheopexy, was noted.

The slips used for viscosity tests were also used for hydrogen-ion determinations with a hydrogen electrode-saturated calomel electrode apparatus. The actual potential of the electrodes was measured by a Leeds and Northrup pH potentiometer connected to a sensitive spotlight galvanometer.

Some tests were made to determine the effect of organic matter. Viscosity tests were made on raw clays which had been treated with hydrogen peroxide solution for several weeks.

Sedimentation tests of clays A, B, F, L, and M were undertaken according to the procedure outlined by Bouyoucos[6] and Casagrande.[7] Grain-size distribution was calculated, using Casagrande's nomographic chart and assuming a gravity of 2.63 for the clay.

(2) Discussion of Results

(*A*) *Electrodialysis:* Clays A, B, C, D, F, L, M, and Q were electrodialized, as well as a sample of Missouri halloysite for comparative purposes. The soft kaolins showed the greatest ease of electrodialysis. Clays A, C, and D showed little or no tendency to disintegrate but reached a practical end point within forty-eight hours. The fact that the lamp bulb in series was very slow in attaining any brilliance indicated a lack of adsorbed ions or a lack of tendency to release them. The relative rapidity with which the operation reached an end point substantiates the former idea. The soft clays remained soft and had little tendency to build a hard crusty layer against the parchment membranes as compared with clays L and Q.

Clay B and clay M showed a strong initial tendency to release ions, inasmuch as the lamp in series with the electrodialysis cell glowed brightly. A longer time was required to reach an end point, and clay B needed more than time clay M. This fact was counter to expectations because clay M was called "hard" and clay B, "semihard," and it was thought that the length of time to reach an end point under constant conditions would increase with hardness.

Clay F showed little tendency to release ions, but it also took a long time (one week) to reach an end point, which suggests that the many adsorbed ions were tightly held. Polyvalent ions would be expected to be difficult to remove from a stable clay mineral such as kaolin. Both raw and electrodialyzed F clays were very dense.

Clays L and Q showed a strong and continuing tendency to release ions. The end points attained even after more than one week were still not so satisfactory as those of the kaolins that were attained much sooner. There was a marked tendency to form a crust of material on the parchment membranes as well as "bridges" through the clay from membrane to membrane. Iron and aluminum compounds were deposited in considerable amount on the copper (negative) electrode. Fine clay was deposited on the platinum electrode, some of which undoubtedly had migrated through the membrane. It was necessary to dismantle the electrodialysis cell and to rework the clay several times before the dialysis was complete.

Comparative tests were run on Missouri halloysite. The behavior of the halloysite was like that of clay F in that ions were released in abundance for some time, but its initial release was much greater. Some material which was deposited on the copper electrode was scraped off and examined under the microscope. This material contained much disseminated aggregate material of fine grain size and low refractive index, but its clay character could not be proved.

(*B*) *Hydrogen Ion and Viscosity Relations:* Viscosity tests were run on untreated clays A, B, C, D, F, L, M, and Missouri halloysite and on electrodialyzed clays A, B, F, L, and M. A range of electrolyte additions was selected in each instance to bring out the individual characters of the clays. The hydrogen-ion concentration of each test specimen was taken, and curves were plotted to show viscosity and pH versus electrolyte addition. The results are shown in Figs. 2 through 8.

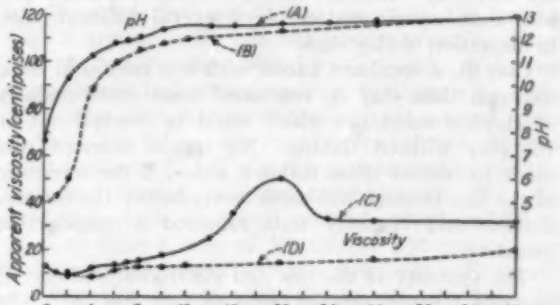

FIG. 2.—Hydrogen-ion and viscosity curves for clay A, a soft kaolin; pH curves, (*A*) on raw clay and (*B*) on electrodialyzed clay; viscosity curves, (*C*) on raw clay and (*D*) on electrodialyzed clay.

Clay A, in the raw condition, contained much muscovite mica and heavy minerals, most of which were removed by screening through 325-mesh. As indicated in Fig. 2, the curves for pH versus electrolyte additions were similar for raw and electrodialyzed clays, with initial pH values of the raw clay somewhat higher. This would indicate the removal of some exchangeable base by the electrodialysis operation. The base-exchange capacity of the electrodialyzed clay at pH 8 was 3 m.e. of NaOH per 100 gm. of clay. Minimum viscosities of the raw and electrodialyzed clays were found at 2 and 4 m.e. per 100 gm. of clay, respectively.

[6] G. J. Bouyoucos, "Comparison Between Pipette Method and Hydrometer Method for Making Mechanical Analyses of Soil," *Soil Sci.*, **38** [5] 335–47 (1934); *Ceram. Abs.*, **14** [2] 44 (1935).

[7] A. Casagrande, Die Araeometer Methode zur Bestimmung der Kornverteilung von Boden (Areometer Method for Determining Grain Distribution in Soils and Other Materials). Julius Springer, Berlin, 1934; 56 pp.; *Ceram. Abs.*, **15** [2] 69 (1936).

The most striking difference between the viscosity behavior of raw and electrodialyzed clay A was the removal by electrodialysis of the "hump" in the viscosity curve. The pH curve had no inflections coincident with this sudden rise and fall of viscosity. This fact suggests some component which does not affect pH but which affects the clay micelle at certain pH values so as to reduce the proportion of water serving as suspending medium to the clay-ionic complex. Norton and Johnson[8] have suggested that organic matter, such as lignite, has this effect. In order to determine the presence and effect of organic matter, the raw clay A was treated with 1% of 30% hydrogen peroxide solution, according to the Norton and Johnson procedure. The slip was shaken frequently during a two-week interval, after which the clay slips were prepared for viscosity tests and electrolyte additions made as before, especially in the range of the peak. It was expected that if carbonaceous matter had caused the hump, removal of the matter by hydrogen peroxide treatment would remove the hump. The viscosity, however, was greatly increased by this treatment, whereas the pH was virtually unaffected. The Norton and Johnson procedure for removal of organic matter was not followed completely because their suggestion of washing with NaOH solution was not used. This step could not be followed without changing the pH of the slip and was therefore omitted. The various viscosity relationships, however, exhibited by the clay in the three conditions (raw, electrodialized, and after treatment of the raw clay with hydrogen peroxide) emphasize the idea that organic matter plays several different roles in dispersion of clay slips.

Clay B, a semihard kaolin with less mica and dark minerals than clay A, contained some small nodules of claylike substance which could be washed out of the clay without slaking. No special attempt was made to remove these nodules, although the screening of the slip through 325-mesh sieves before the electrodialysis and viscosity tests removed a considerable quantity.

The viscosity of the raw and electrodialyzed clay B samples showed erratic behavior (see Fig. 3). The saturation capacity of the electrodialyzed clay at pH 8 was 11.3 m.e. per 100 gm. The minimum viscosity of this clay was apparently at zero addition of electrolyte, and the inflection of the pH curve occurred simultaneously with a pronounced peak in the viscosity curve. A strong tendency to gel, both as thixotropy (gelation on standing) and rheopexy (gelation quickened by rhythmic motion, such as tapping or twirling) was noted with NaOH additions of about 11 m.e.; 20 m.e. of NaOH per 100 gm. brought the viscosity of the electrodialyzed clay down to a second minimum. This minimum in the raw clay was higher and at a greater electrolyte content. It is possible that the minimum viscosity was coincident with a minor inflection of the pH curve and that

[8] F. H. Norton and A. L. Johnson, "Fundamental Study of Clay: I, Preparation of Purified Kaolinite Suspension," *Jour. Amer. Ceram. Soc.*, **24** [2] 64–69 (1941).

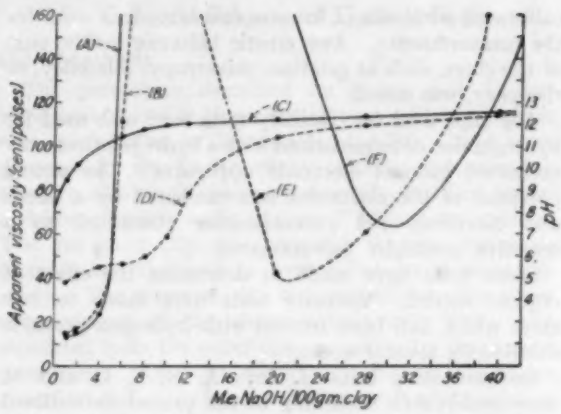

FIG. 3.—Hydrogen-ion and viscosity curves for clay B, a semihard kaolin; viscosity curves, (*A*) and (*F*) on raw clay, (*B*) and (*E*) on electrodialyzed clay; pH curves, (*C*) on raw clay and (*D*) on electrodialyzed clay.

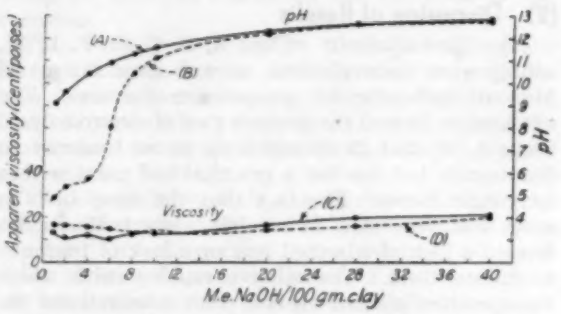

FIG. 4.—Hydrogen-ion and viscosity curves for clay M, a hard kaolin; pH curves, (*A*) on raw clay and (*B*) on electrodialyzed clay; viscosity curves, (*C*) on raw clay and (*D*) on electrodialyzed clay.

a double inflection of the pH curve was caused by the presence of another mineral or substance of different saturation capacity. In contrast to the curves for clay A, however, the peak of viscosity with clay B was coincident with a marked inflection of the pH curve.

Clay M, a hard kaolin with little mica or dark minerals, contained a large amount of nodules of a claylike substance similar to the nodules in clay B. The viscosity curves of raw and electrodialyzed clays were similar (see Fig. 4), and it is striking that electrolyte additions up to 40 m.e. per 100 gm. of clay altered the viscosity very little. The base-exchange capacity at pH 8 was 6 m.e. per 100 gm. of clay. A slight minimum in the viscosity curve occurred coincidently with an inflection in the pH curve. No hump of appreciable proportions was noted in the viscosity curve at any electrolyte addition. This fact raises the question as to whether the substance or condition causing the humps in the viscosity curves of clays A and B was missing or was masked.

The raw sample of clay L, a fuller's earth contaminated with such admixture minerals as quartz, cristobalite, mica, calcite, iron carbonates, and other heavy minerals, was gritty and much stained by

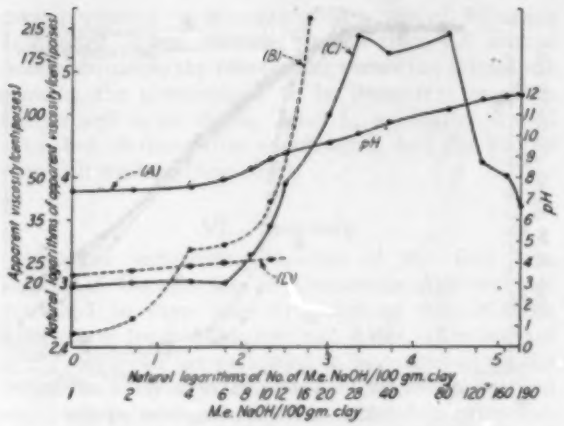

FIG. 5.—Clay L, fuller's earth; slip contains 300 cc. of water per 100 gm. of clay; curve (*A*), pH of raw clay; curve (*B*), apparent viscosity of electrodialyzed clay; curve (*C*), apparent viscosity of raw clay; and curve (*D*), pH of electrodialyzed clay.

pyrolusite on different laminae. When wet, the raw clay had a soapy feel and an apple-green color, and it dried to a yellowish gray color. Screen tailings included a considerable amount of dark minerals, mica, and quartz and a quantity of very small, unslakable yellow nodules. These nodules were of the same clay substance as the mass as far as could be determined. They were different in size and color from those in clays B and M but similar in shape and in resistance to slaking. Clay L showed a marked swelling and behaved in typical bentonitic fashion (Fig. 5). It was found that 7 m.e. per 100 gm. of electrodialyzed clay caused a gel formation thick enough to prevent viscosity measurements with the 150-gm. weight on the pan of the viscosimeter, and it was necessary to dilute the slip to obtain a viscosity curve. With added water (50% more than the original amount), measurements were made up to 16 m.e. of NaOH per 100 gm. The raw clay showed a somewhat different behavior, having a measurable viscosity up to 28 m.e. of NaOH per 100 gm. of clay in the dilute suspension. The viscosity of the raw clay tended to drop at 120 m.e. of NaOH per 100 gm., in which respect it differed from the electrodialyzed clay even up to 400 m.e. per 100 gm. The pH values of the electrodialyzed clay were not obtained up to base-exchange capacity because of the thick gel formed before this point was reached. Measurements would have necessitated several hundred per cent of dilution and considerable agitation. The base-exchange capacity was obtained by titrating the hydrogen ions to pH 8 after treating with an excess of barium chloride solution. The value thus obtained was 50 m.e. per 100 gm. of clay.

Clay F, a clay found in a pit of soft kaolin, occurs as large barrel-like concretions which are much denser and harder and more tan-colored than the surrounding kaolin; it is neither stratified nor permeable to water. The clay boulders, which remain in place in the pit after the kaolin is removed, break up into small blocky lumps of conchoidal fracture. The clay

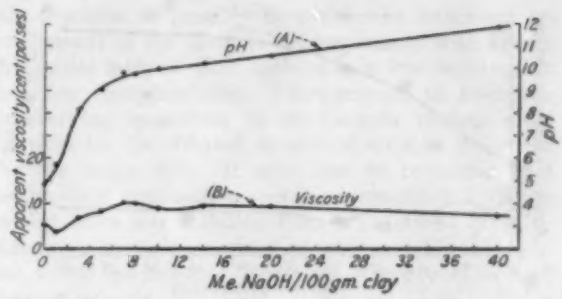

FIG. 6.—Clay F, raw; 10 gm. of clay per 100 gm. of liquid; (*A*) pH curve and (*B*) viscosity curve.

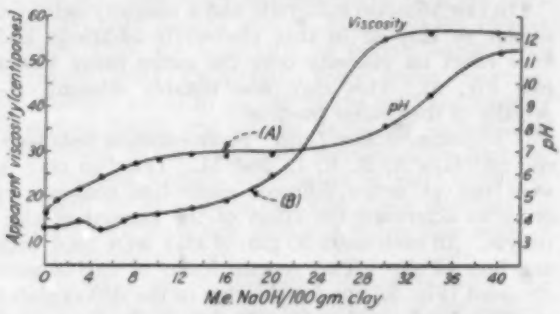

FIG. 7.—Clay F, electrodialyzed; slip, which is less dilute than previous samples, contains 20 gm. of clay per 100 gm. of water; (*A*) pH curve and (*B*) viscosity curve.

is discarded because it contaminates the kaolin. Clay F ground easily to a fine powder, which appeared almost greasy when mixed with water. The clay mass seemed to have no tendency to disperse itself but after dispersion by mechanical means seemed quite stable. The clay, raw or electrodialyzed, showed great tendency to gel, which was decreased by electrodialysis. Treated as were other kaolins, the clay swelled to such an extent with electrolyte additions of more than 8 m.e. of NaOH per 100 gm. of clay that the usual ratio of clay to water could not be used. A determination was made on the viscosity behavior of a slip containing 10 gm. of raw clay per 100 gm. of water (see Fig. 6). Minimum viscosity in this curve was coincident with an inflection in the pH curve. A slight hump was noted in the viscosity curve, followed by a gradual decrease in viscosity for the remainder of the electrolyte additions. Because the suspension appeared to be unnecessarily dilute, the electrodialyzed clay was tested in a slip containing 20 gm. of clay per 100 gm. of water (see Fig. 7). It is notable that there was a minimum in viscosity coincident with an initial inflection in the pH curve between 4 and 5 m.e. of NaOH per 100 gm. of clay. The main inflection in the pH curve was at 33 m.e. per 100 gm. of clay (the saturation capacity at pH 8) coincident with a peak in the viscosity curve.

The "soft" clays, C and D, were tested only in the raw condition; their curves are somewhat similar to curves for clay A, and no very erratic behavior was noted.

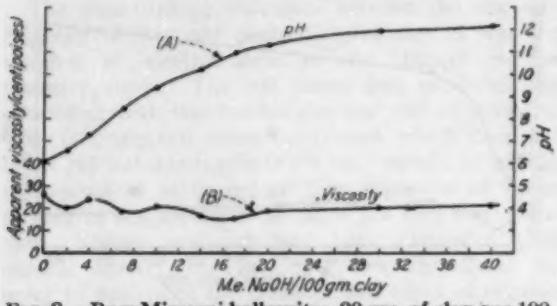

FIG. 8.—Raw Missouri halloysite; 20 gm. of clay per 100 gm. of liquid; (*A*) pH curve and (*B*) viscosity curve.

The raw Missouri halloysite had a viscosity behavior similar to clay M in that electrolyte additions had little effect on viscosity over the entire range tested (see Fig. 8). This clay was notably dilatent, especially in the coarser fraction.

(*C*) *Sedimentation Tests:* Sedimentation tests were run on clays A, B, F, L, and M. Tests on clay A were run at seven different electrolyte contents in order to determine the effect of the amount of electrolyte. In each case, 50 gm. of clay were used with one liter of slip. Two general forms of curves were obtained (Fig. 9), one for the clay in the deflocculated condition and another for the clay in the flocculated condition. At some electrolyte contents, all grain sizes seemed to be either flocculated or dispersed; at other concentrations, only the larger grains were flocculated and the finer fractions remained dispersed. The slip was deflocculated with 0, 2, 6, 10, and 14 m.e. and flocculated with 20, 26, and 34 m.e. of NaOH per 100 gm. of clay. Of all the electrolyte additions, 10 m.e. per 100 gm. seemed to give the best deflocculation of this clay. Increasing the NaOH to 14 m.e. per 100 gm. seemed to start flocculation of the larger grains, whereas flocculation of most of the clay was complete with 20 m.e. per 100 gm. It is logical to assume that the curve that showed best deflocculation was most truly representative of the actual grain-size distribution. Clay A was accordingly considered to have a uniform gradation of grain sizes between diameters of 0.5 and 10 microns with about 75% of material smaller than 5 microns and about 25% finer than 0.5 micron.

The flocculation and deflocculation of clays B, F, L, and M during sedimentation were observed in a similar manner, but only the curves representing the most complete deflocculation found were plotted for comparison in Fig. 10.

Clay B showed deflocculation with zero and 8 m.e. and reflocculation with 20 m.e. of NaOH per 100 gm. of clay. Approximately 75% of this clay was smaller than 5 microns and 30% had diameters of less than 0.5 micron.

Clay F showed flocculation with zero and 4 m.e. and deflocculation with 12 and 20 m.e. of NaOH per 100 gm. of clay. This clay seemed to be about 60% finer than 0.5 micron and 95% finer than 5 microns.

Clay L was flocculated in water and partially deflocculated with 6 m.e. of NaOH per 100 gm. Approximately 85% was finer than 5 microns and 30% was indicated as being finer than 0.5 micron. With this particular clay, however, complete dispersion probably was not effected because the slip contained fine nodules extremely difficult to disperse although they were composed of particles of finer ultimate particle size. The values obtained, therefore, may be too small.

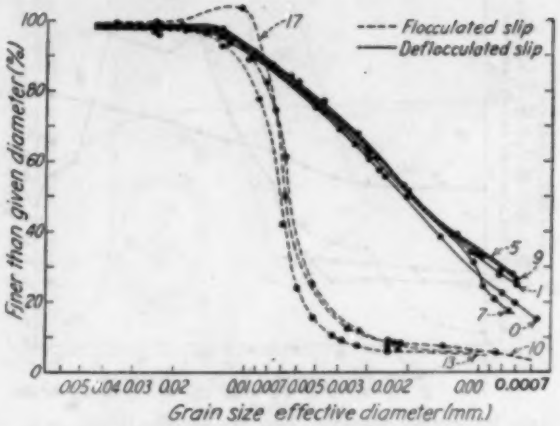

FIG. 9.—Clay A, soft kaolin; apparent grain-size distribution with different amounts of electrolyte; the curve number also indicates the number of m.e. of NaOH per 50 gm. of clay in 1000 cc. of suspension; deflocculated slip curves, (5) pH 9.26; (9) pH 9.02; (1) pH 8.65; (7) pH 9.65; (0) pH 8.06; flocculated slip curves, (10) pH 10.02; (17) pH 10.28; and (13) pH 10.12.

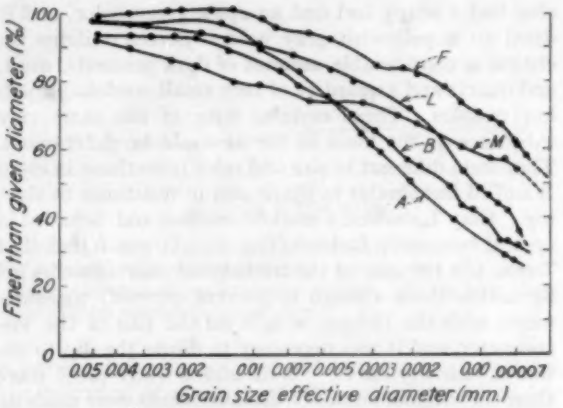

FIG. 10.—Comparative grain-size distribution curves for deflocculated slips made from clays F, M, L, B, and A.

Clay M showed deflocculation with 0, 12, and 20 m.e. and reflocculation with 40 m.e. of NaOH per 100 gm. of clay. About 75% was finer than 5 microns and 50% finer than 0.5 micron.

(*D*) *Stream Birefringence:* Clays A, B, C, D, F, L, and M were examined for stream birefringence. This was done by twirling a beaker of dilute slip between crossed polaroid disks. The appearance of interference colors in definite patterns showed that the particles were not spherical but were aligned so that a major axis was parallel to the axis of rotation. All of the clays showed weak interference colors, but

none compared in intensity with a slip of Wyoming bentonite. When particles larger than 0.5 micron were eliminated, the effects were somewhat intensified, showing the phenomenon to be dependent on grain size as well as on shape. Clay L, especially, showed a marked increase after centrifuging, but the kaolins were still weak in their effect.

VI. Summary

(1) The sedimentary kaolins of the Fall Line Region of Georgia are of Cretaceous Age and are presumed to have been deposited in still off-shore lakes where fresh water met salt water. Electrolytes of the salt water are presumed to have flocculated the extremely finely divided clay matter, which settled out (perhaps even as alumina-silica gels), contaminated with other soluble ingredients and showing local variation. Subsequent crystallization is postulated to have proceeded by stages, controlled by local conditions to some extent. The hard kaolins are of extremely fine grain size and have not yet reached a high degree of crystallinity. Soft clays, on the other hand, are much coarser and show greater crystallinity.

(2) The chemical analyses of the clays investigated show that all clays regarded as kaolins are rich in alumina and are deficient in silica even beyond the kaolinite ratio. This would indicate that a mineral of the kaolinite group, stable in the presence of excess alumina, was formed under the conditions which have existed since deposition.

(3) The low content of iron oxide and magnesia is consistent with a conclusion that montmorillonite is not present to a great extent, if at all, in the commercially mined kaolins. One clay tested (clay F) showed some indications of having montmorillonite as a contaminant.

(4) The morin tests indicate that aluminum ions are released more readily from some clays than from others. In comparison with Zettlitz kaolin, which shows no solubility of alumina in this test, soft kaolins show little and hard clays show more. This variation in solubility points to a different degree of bonding of the alumina or possibly to a different structural arrangement of the alumina. Comparisons with known halloysite suggest that halloysite is less resistant to solution than kaolinite. The presence of halloysite in varying quantities in the Georgia kaolins could account for the different degrees of stability evidenced by the morin test. It may also be presumed that amorphous material or poorly crystallized kaolinite would have less stability than well-formed crystals. Likewise, amorphous gels or poorly crystallized kaolinite would presumably have less stability than well formed crystals.

(5) The electrodialysis behavior of Georgia kaolins likewise indicates different degrees of stability. Soft kaolins are more easily electrodialyzed than are semihard and hard kaolins and much more easily electrodialyzed than are bentonitic or fuller's earth types of clays. With these latter clay types, however, the stability seems to depend on the type and number of surface bonds and on the degree of isomorphous replacement rather than on the bonding of the alumina.

(6) Georgia kaolins are classed as soft, semihard, and hard by the producers, and these designations correlate with grain size, that is, a coarse clay is softer than a fine-grained clay.

(7) Correlation of viscosity behavior with the designations of hard, semihard, and soft is not perfect. Erratic viscosity relations may result from a peculiar distribution of grain size, the presence and nature of organic matter, mineral admixture, and grain shape. If semihard clays in general are classed with the hard, fairly characteristic viscosity behavior may be ascribed to hard and soft kaolins. A general relationship is found between the base-exchange capacity and the hardness of the clays. Soft kaolins have small saturation capacity; the semihard and hard kaolins, more; and the fuller's earths, the largest capacity.

(8) The characteristics brought out by geological evidence and by chemical and colloidal analyses have been correlated with evidence obtained from mineralogical analyses, which is discussed in Part II of this paper.

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NATURE OF GEORGIA KAOLINS: II, EVIDENCE OF MINERALOGICAL ANALYSIS*

By Lane Mitchell and E. C. Henry

Abstract

Samples of Georgia kaolins were investigated by thermal analysis and by X-ray and microscopic examinations. Soft kaolins were found to have a high percentage of crystalline kaolinite, whereas hard kaolins contained substantial amounts of less crystallized material. Variations in the degree of crystallization, grain size, nature and amount of organic matter, and admixture of different minerals are given as reasons for the differences in the clays examined.

I. Introduction

In Part I† of this study of Georgia kaolins, the selection of samples used in this investigation was discussed and a résumé of the geologic background of the clays and the evidence of chemical and colloidal analyses concerning their nature were presented. The studies for Part II have involved mineralogical investigation by the usually accepted methods, including

* See star (*) footnote, p. 105.
† This issue, pp. 105–13.

microscopic and X-ray examinations and thermal analyses. The conclusions drawn from this work are consistent with the interpretations of the chemical and colloidal analyses and geological investigation.

(1) Nomenclature

Clay minerals of slightly different properties for many years were known by a wide variety of mineral names, many of which even today are encountered in the literature. Most investigators and writers on the subject agree that clay minerals may be classified into three groups, namely, the kaolinite, the montmorillonite, and the illite or hydrous mica groups.

(2) Origins

The origins of the different types of clays are many and varied. Kaolinite is generally a result of weathering, but possible hydrothermal varieties are known. Nacrite and dickite, as far as is known, have hydrothermal origin. Anauxite, halloysite, and allophane are usually ascribed to weathering processes. The formation of the montmorillonites has been most widely attributed to the weathering of volcanic ash, but many investigators have reported other possible origins, such as the hydrochemical alteration of feldspar, the weathering of pegmatite dikes, and authigenic growth in soils. Grim[1] says that illite minerals form under undetermined conditions, but the prime mode of origin probably is in diagenetic processes.

(3) Mineralogical Background of Georgia Kaolins

The Georgia kaolins have been generally supposed to consist of kaolinite. As these clays are clearly of sedimentary origin and as they have undergone little diagenesis or change into solid rock, it seems unlikely that the clay minerals nacrite, dickite, or illite would be found. Inasmuch as the chemical analyses of the clays do not show excessive iron or magnesium, the presence of nontronite and saponite in considerable amount is excluded. The plastic properties of montmorillonite, moreover, are well known, and a comparison suggests that this material at least is not the primary constituent. The major clay mineral constituents, namely, kaolinite, halloysite, anauxite, and allophane therefore remain for consideration. Chemical analyses rule out anauxite in most of the clays, inasmuch as the SiO_2 to Al_2O_3 ratio is less than 2; clay F has a ratio of 2.26, but this ratio includes any free silica present. It is to be expected, therefore, that only kaolinite, halloysite, or allophane might be found in substantial amounts in the kaolins. The possibility of lesser amounts of the other clay minerals is not entirely excluded, particularly montmorillonite, whose presence in the overlying fuller's earth has suggested the possibility that it has contaminated the kaolin underneath. Small amounts of montmorillonite, anauxite, beidellite, nontronite, saponite, or illite would be difficult to observe because their identities would likely be masked in an abundance of kaolinite, halloysite, or allophane.

[1] R. E. Grim, "Properties of Clay," p. 487 in Recent Marine Sediments, a Symposium, pp. 466–95. Published by American Assn. of Petroleum Geologists, 1939; *Ill. Geol. Surv. Circ.*, No. 49, p. 487, 1939; *Ceram. Abs.*, **20** [3] 76 (1941).

II. Microscopic Examination of the Samples

Permanent mountings of a sample of each clay were made with Hyrax mounting medium, which has an index of refraction of 1.7135. This material was chosen instead of Canada balsam in order to bring out relief more sharply. Artificial light with blue glass filters was used for illumination, and the following observations were made:

Clay A contained good kaolinite crystals and showed a development of kaolinite from amorphous and aggregate material. The heavy and coarse minerals which accompany this clay are such as may have been derived from pegmatites. The heavy minerals are not assumed necessarily to have the same origin as the clay material.

Clay B showed a development of "quasicrystals," which consist of disseminated aggregate material having a vague crystal outline. This material is of lower refractive index than kaolinite and stands out in marked contrast to the clear kaolinite crystals. Authigenic development (growth in place) of kaolinite was shown by the presence of curved, cross-fractured crystals called "shrimp" or "worms." Such fragile forms as these shrimp could not have traveled far without being torn apart. Their presence therefore leads to the almost inescapable conclusion that they have grown since deposition of the clay material. The occurrence together of clear kaolinite crystals and aggregate material of lower index suggests that the clay consists of a mixture of clay minerals.

Clay C had thinner flakes of kaolinite than any other clay tested. The condition of the flakes gave the appearance of an incomplete development of kaolinite from amorphous material without a prominent intermediate step and demonstrates the possibility of a clay consisting of very thin flakes of relatively large cross-sectional area.

Clay D revealed a similar development of kaolinite to that of clay C, but it also indicated authigenic origin by the presence of many shrimp.

Clay F was a development of an intermediate stage between the clear kaolinite crystals and an aggregate material of lower index. Electrodialysis electrode deposits accentuated this difference; the material of higher index, which was deposited on the positive electrode, apparently was kaolinite whereas that on the negative electrode appeared to be a mineral of much lower index, resembling halloysite. There was some evidence in the raw whole sample that the two varieties grade into each other. In a number of instances, an aggregate was attached with optical continuity to a clear crystal of different index. The lack of heavy minerals suggests a growth from amorphous material, chemically flocculated.

Clay M consisted of aggregate matter more widely disseminated than in the other kaolins; it was apparently an admixture of at least two clay minerals, the most plentiful of which had an index of approxi-

mately 1.565 whereas that of the other was slightly lower than 1.54.

Clay L seemed to consist of montmorillonite and accessory minerals, including quartz, mica, zircon, ilmenite, magnetite, rutile, calcite, and staurolite.

III. Thermal Analysis

(1) General Considerations

If a clay substance is heated at a uniform rate under oxidizing conditions, a number of phenomena take place, chiefly the loss of water, mechanically or chemically combined. If carbonaceous or sulfurous matter is present, oxidation may be expected; if free quartz, chert, or opaline silica are present, inversions may be found. There are possible changes in accessory minerals, and the breakdown of the crystal structure of the clay itself will result in a recombination of oxides and crystallization into different minerals.

These processes involve either endothermic or exothermic effects. In clay minerals of relative purity, the effects of oxidation, inversions of silica, and changes of accessory minerals are relatively small compared to the effects resulting from the loss of water. Dehydration behavior has been found to be characteristic of the clay minerals involved and therefore may be used as a means of identification. Two methods of measurement are possible, namely, direct measurement of loss of water with temperature or measurement of the heat effects involved at various temperatures; both methods involve a constant rate of heating.

The differential thermocouple method[2] is well established; one junction of the thermomocouple is inserted in the sample to be tested and the other in an inert reference substance which shows no heat effects. If both substances are heated together at the same constant rate, a lag in temperature of the unknown material behind the reference material indicates an endothermic effect whereas a lead indicates an exothermic effect. It is to be emphasized that this latter method of thermal analysis is not a direct measurement of physical structure; rather, it measures the energy required for release of water or the energy released in the crystallization of component oxides and crystallographic inversion. The effects of admixed materials in small quantity are often obscured or negligible.

A steady heating rate obviously must be maintained in order that the speed with which a given process arrives at equilibrium will be characteristic of the material. If the rate were infinitely slow, equilibrium would be attained at every instant and no differential temperature between sample and inert substance would be observed.

(2) Apparatus and Method

A small chrome steel block was prepared to hold in each of two holes or compartments, side by side and only 4 mm. apart, about 3.5 cc. of material. These compartments were approximately 13 mm. in diameter and 18 mm. deep. Small holes were bored into the centers of the side walls of these cylindrical spaces, through which thermocouple wires were introduced into the clay and inert substance. The wires were insulated with porcelain spacers, and the assembly was so constructed that couples and insulation were permanently fixed in the shape of the letter F and could be introduced or withdrawn at will. The couple was of the three-lead type and was made of Chromel-Alumel, two leads being of Chromel and the third of Alumel. Insulated from each other, all wires led to a Dewar flask where U tubes containing mercury were immersed in ice and where contacts were made with leads from a potentiometer.

A small Nichrome-wound electric furnace was used. The heating chamber consisted of a fused alumina muffle, approximately 2 in. in diameter and 12 in. long. Plugs, made of insulating brick, were fitted into each end of the muffle, each plug extending approximately $3^1/_2$ in. into the furnace. One plug was grooved to hold the thermocouple leads.

Furnace temperatures were controlled manually by an induction regulator to maintain a steady rise of 14° ± 3°C. per minute. Thermocouple millivolts were determined with a sensitive potentiometer. To eliminate the possibility of back currents, the reading of the differential couple was made a few seconds before that of the absolute couple, with the double circuit open in each case. Results were recorded against time, and curves of galvanometer-scale divisions against temperature and time against temperature were plotted.

A number of tests showed that errors are introduced in a curve through inherent characteristics of the apparatus, differences between specific heats of specimen and reference material, and differences in packing and shrinkage. Most of these errors could be compensated for by making a second run on the calcined material without disturbing the setup. A subtraction of the curve of the second run from that of the first run produced a curve which eliminated most inherent errors except that caused by differential shrinkage. Even where appreciable shrinkage occurred, a zero datum was much more closely approached than in the curve of the initial run alone (see Fig. 1). Several runs showed that the method gave results of high reproducibility.

(3) Results of Thermal Analyses

All of the clays tested showed heat effects (see Figs. 2 and 3). All samples, except the montmorillonites and fuller's earth, showed exothermic effects of considerable extent near 980°C., which is believed to be a definite indication of the presence of minerals of the kaolinite group. Clays A, B, C, D, F, M, A fines, M fines, M nodules, and Zettlitz kaolin showed strong

[2] (*a*) The differential thermocouple technique was first used by Roberts Austen prior to 1900 and was first applied to a ceramic problem (the inversion of cristobalite) by C. N. Fenner of the Geophysical Laboratory, Washington, D. C.; see *Z. anorg. Chem.*, **85**, 169 (1914).

(*b*) F. H. Norton, "Critical Study of the Differential Method for Identification of the Clay Minerals," *Jour. Amer. Ceram. Soc.*, **22** [2] 54–63 (1939).

endothermic effect at points between 610° and 650°C., which corresponds well with published data for kaolinite.

Clays B, F, M, M nodules, M fines, and clay L, however, also showed low-temperature peaks around 150°C. as did the Indiana and Missouri halloysites and the Mexican montmorillonites. Clays A, A fines, C, and D showed only slight endothermic effects in this region. Characteristic gibbsite peaks around 350°C. were noted in the two known halloysites tested, but these peaks were not very noticeable in any of the kaolins. Small peaks in this vicinity were noted with clay A, clay A fines, clay C, M nodules, and M fines and were possibly masked in clays D, F, and M by other effects.

Clays C, D, F, and M failed to return to the datum line between early and major endothermic effects. This effect suggests a continuous loss of water, which is characteristic of allophane.

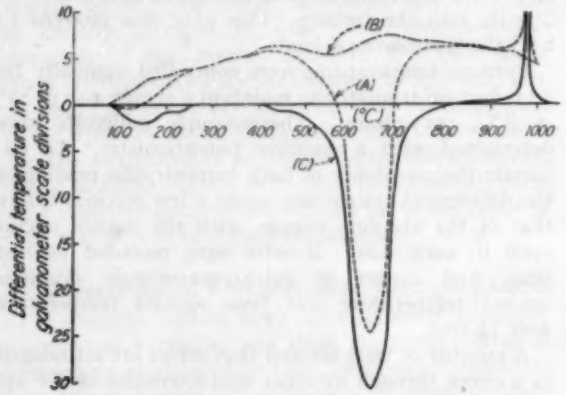

FIG. 1.—Thermal analysis of clay A; curve (*A*) original data; curve (*B*) data on rerun; curve (*C*) corrected data.

Structure in the low-temperature endothermic effects is usually considered to be characteristic of montmorillonite. Structures occurred in the low-temperature effects of all the Georgia kaolins tested, but in clays B, C, D, M, M nodules and M fines, and of course, clay L, they resembled structures in montmorillonite curves obtained by Norton[2(b)] and by the writers. Such structure might have been caused by a small admixture of allophane and halloysite or poorly crystallized kaolinite.

Norton's curves for bentonite and china-clay mixtures showed mutual repressing of the heat effects of the constituents in proportion to the amount of admixture, but clay F showed two deep endothermic peaks, neither of which seems to be greatly repressed at the expense of the other.

The curve for clay L more closely resembled Norton's curve for beidellite than his or the writers' curves for montmorillonite, but the latter mineral is known to give variable results in this test. Montmorillonite rather than beidellite is indicated by other evidence.

An admixture of gibbsite with kaolinite might give curves similar to those of halloysite. Admixtures of diaspore or bauxite with kaolinite might give structure

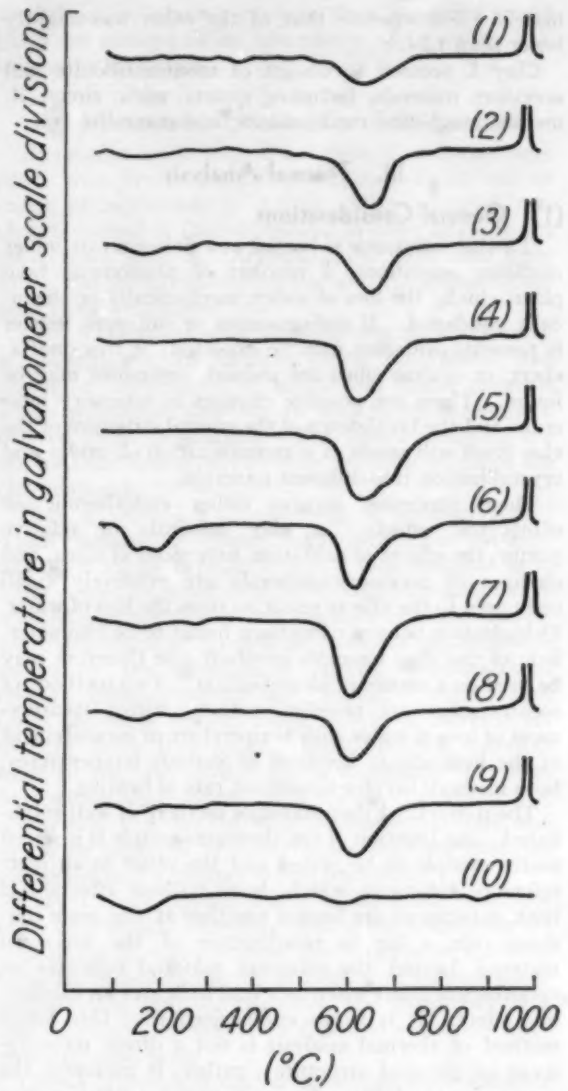

FIG. 2.—Thermal analysis of test clays: curve No. (1) clay A, fines; No. (2) clay A, soft kaolin; No. (3) clay B, semihard kaolin; No. (4) clay C, soft kaolin; No. (5) clay D, soft kaolin; No. (6) clay F, hard concretionary clay; No. (7) clay M, hard kaolin; No. (8) clay M, nodules; No. (9) clay M, fines; No. (10) clay L, fuller's earth.

to the return curve from the major endothermic peak. Gibbsite, diaspore, and bauxite, however, were not identified under the microscope.

IV. X-Ray Analysis

(1) Technique and Apparatus

A simple and satisfactory technique for the examination of powders by X-ray methods involved the use of a small cylindrical camera with a channel slit in the cylinder wall through which X rays could enter and strike a sample of powder. The powder was mounted with Canada balsam on a copper wire held in the cylindrical axis by a hub penetrating the lid of the

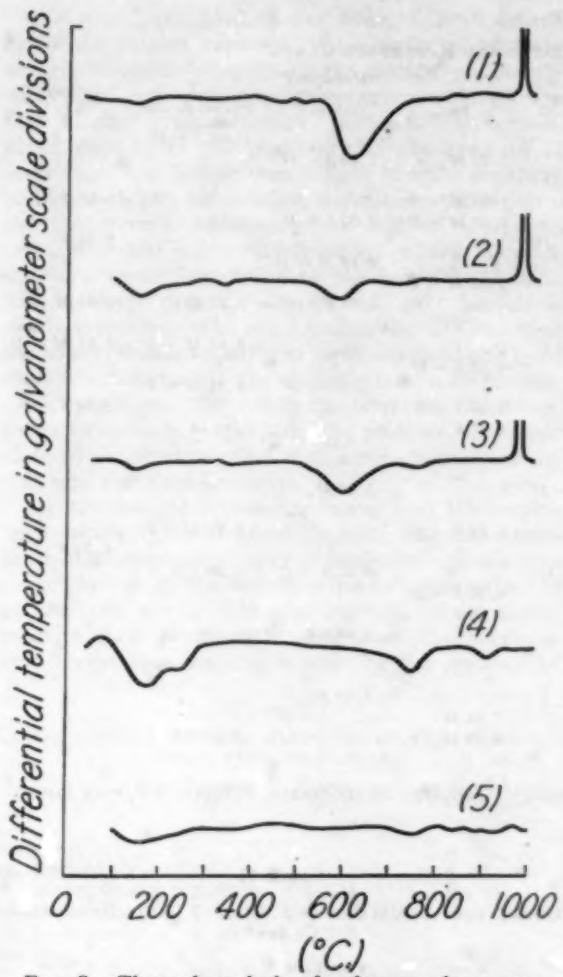

FIG. 3.—Thermal analysis of reference clays: curve No. (1) Zettlitz kaolin; No. (2) Bedford, Indiana, halloysite; No. (3) Missouri halloysite; No. (4) Vera Cruz, Mexico, montmorillonite; No. (5) Mexican montmorillonite.

camera. The film to record the spectrum was wrapped around a flange of the lid concentric with the wire and was held firmly by a rubber band. The loaded camera was exposed by placing it before the window of an X-ray tube.

The apparatus used in this investigation consisted of two cameras and an X-ray tube using copper radiation, CuKα, and CuKβ. Results of investigations are generally recorded in the literature in terms of d values. With given cameras, however, and the use of the same procedure throughout, patterns of unknowns may be compared directly with patterns of knowns in terms of L values, which are the distances between similar lines on a pattern. These L values are satisfactory only for comparative purposes. Corrections may be made for any shifting of L distances by correcting the L values for copper lines on the same film and interpolating. If comparison with published data is desired, L values may be converted to θ values by the formula,

$$L/2r = 4\theta/360°$$

r = radius of camera flange around which film is wrapped.

With θ known, calculation of d values is made by the Bragg formula

$$n\lambda = 2d \sin \theta$$

Wave length of copper Kα radiation = 1.532 a.u.

(2) Results of Tests

X-ray diffraction patterns of clays A, B, F, L, and M were made and were compared with patterns made under the same conditions for the following reference materials: Zettlitz kaolin, Missouri halloysite, Cornwall, Pa., halloysite, Djebel de Bar halloysite,[3] Wyoming bentonite, and Vera Cruz montmorillonite. L values were read from the films for all lines, including those of copper. By comparing the observed L values of copper with theoretical values, a curve could be plotted to show variations at different points. Values for other lines were corrected by interpolating on this curve. Not all d values were calculated because a direct comparison of L values was sufficient in most cases. The d values for clay A were checked against published data and agreed well. Ross and Kerr[4] have stated that differentiation between lines for halloysite and kaolinite was most effective in the range of lines representing spacings between 4 and 3.4 a.u., and d values were therefore calculated for all the kaolins and halloysites and clay L in this region. Agreement with published data was not very good. Some spacings for halloysite given by Ross and Kerr[4] compared more favorably with kaolinite d values obtained here and vice versa. These discrepancies were not large, but they made positive identification confusing. The results are given in Table III. Table I shows a comparison of L values for all the kaolins tested as well as for clay L, Zettlitz kaolin, and the three halloysites. Table II gives a comparison of L values for clay L, Vera Cruz montmorillonite, Wyoming bentonite, and cristobalite. The data given in Table I show fair agreement between the values for the commercial kaolins, clay F, and Zettlitz kaolin and indicate the presence of a common mineral, presumably kaolinite. The values for the halloysites were not greatly different, and a positive distinction could not be drawn. In comparison with known pure halloysite the Djebel de Bar material and all of the Georgia kaolins give L values not widely different.

V. Discussion of Nature of Georgia Kaolins

A critical examination of the conclusions reached after studying separately the evidence of geological origin, deposition, and sedimentation, chemical analysis, colloidal behavior, grain-size distribution, and mineralogical makeup as determined by microscope, X-ray and thermal analyses, leads to the establishment of

[3] M. Mehmel, "Structures of Halloysite and Metahalloysite," *Z. Krist.*, **90**, 35–43 (1935); *Ceram. Abs.*, **14** [11] 291 (1935).

[4] C. S. Ross and P. F. Kerr, "Halloysite and Allophane," *U. S. Geol. Surv. Prof. Paper*, No. 185-G, 13 pp. (1934); *Ceram. Abs.*, **14** [4] 101 (1935).

TABLE I

CORRECTED *L* VALUES FOR CLAYS TESTED AND REFERENCE CLAYS*

Zettlitz kaolin	Clay A	Clay B	Clay F	Clay M	Halloysite Pa.	Halloysite Mo.	Halloysite Djebel de Bar	Clay L
				1.12 *F*			0.95 *S* – *D*	
	1.20 *S* – *D*	1.20 *VF*	1.23 *F*		1.22 *M*	1.25 *S* – *D*		
1.27 *S*	1.30 *F*	1.30 *F*	1.30 *S*	1.27 *S* – *D*				
	1.52 *F*			1.43 *M*	1.64 *M* – *D*			1.67 *F*
2.07 *F*			2.07 *M*		2.10 *M* – *D*	2.09 *S* – *D*	2.11 *S*	
	2.24 *M*	2.19 *F* – *D*		2.22 *M* – *D*				2.28 *S*
						2.49 *M* – *D*		
2.54 *S*	2.59 *S*	2.55 *S*	2.54 *S*	2.51 *S*	2.53 *M* – *D*			
						2.74 *F* – *D*	2.71 *M*	2.87 *M*
3.24 *F*	3.31 *VF*	3.27 *VF*		3.20 *F*				
3.60 *S* – *D*	3.63 *M* – *D*	3.63 *M* – *D*	3.62 *M* – *D*	3.60 *M* – *D*			3.63 *M* – *D*	3.61 *M* – *D*
				4.10 *F*	4.13 *S* – *D*			
	4.20 *VF*		4.29 *F*				4.21 *M* – *D*	
					4.36 *S* – *D*			4.36 *S* – *D*
					4.37 *S*			
4.67 *F*		4.66 *VF*		4.61 *F*				
			5.25 *F*					
5.63 *S* – *D*	5.60 *M* – *D*	5.60 *M* – *D*	5.66 *F* – *D*	5.62 *M* – *D*		5.69 *M* – *D*		
	5.70 *VF*							
					5.72 *F* – *D*		5.78 *M* – *D*	
6.09 *VF*	6.05 *VF*							6.22 *F*
6.31 *S*	6.29 *M*	6.31 *M*	6.32 *M*	6.32 *S* – *D*		6.35 *S* – *D*	6.40 *S* – *D*	
				6.48 *VF*	6.41 *F* – *D*			
					6.64 *F*			
			6.96 *F*			6.88 *VF*		
	7.12 *VF*							
7.33 *VF*	7.29 *VF*							
7.77 *F* – *D*	7.77 *F* – *D*	7.82 *F*		7.77 *F* – *D*		7.76 *M*		
					7.96 *M*			
					8.36 *M*		8.42 *VF*	
			8.74 *VF*					

* The letters which follow the values have the following meanings: *S*, strong; *M*, moderate; *F*, faint; *VF*, very faint; and *–D*, diffuse.

certain opinions, apparently supported by a complete correlation of evidence.

(1) The geological evidence establishes the age of the kaolins as Upper Cretaceous and the source material as feldspathic. On the basis of lack of sizing and of bedding, there is strong indication that the clays were deposited by flocculation caused when fresh water met salt water.

(2) The chemical evidence shows that minerals of the kaolinite group should be most abundant in these clays, inasmuch as the silica-alumina ratio would permit only a negligible content of montmorillonite or other clay minerals. One clay, which has a larger silica content and more iron and magnesia, probably has other clay minerals and accessory materials mixed with its kaolinite. Morin dye tests indicate the presence of soluble alumina in all of the kaolins tested, but there is much less in the soft clays than in the semihard and hard kaolins. Fuller's earth and Zettlitz kaolin, according to this test, did not release alumina, whereas halloysite showed a considerable reaction with morin. Because of its amorphous character, allophane also would be expected to show a positive test for aluminum ions. It would seem, therefore, that the harder Georgia kaolins contain more material of the nature of poorly crystallized kaolinite, halloysite, or allophane than do the soft clays.

(3) Regarding the colloidal behavior of the clays tested, the soft clays have small saturation capacity,

TABLE II

CORRECTED *L* VALUES FOR CLAY L AND REFERENCE CLAYS*

Wyo. bentonite	Vera Cruz montmorillonite	Clay L	Cristobalite†
		1.67 *F*	
	1.76 *F*		1.81 *F*
2.07 *M*	2.01 *S* – *D*		2.04 *S*
		2.28 *S*	2.21 *S*
2.75 *M*			
2.92 *F*	2.88 *M* – *D*	2.87 *M*	2.86 *M*
			3.14 *M*
			3.27 *S*
			3.47 *VF*
3.61 *S* – *D*	3.60 *S* – *D*	3.61 *M* – *D*	3.64 *S*
3.77 *M* – *D*			
			3.87 *VF*
			4.70 *F*
			4.89 *F*
			5.42 *F*
5.61	5.69 *M* – *D*		
			5.76 *M*
6.10 *VF*			6.09 *F*
		6.22 *F*	6.24 *F*
6.34 *M*	6.39 *S*		
			6.56 *F*
6.90 *F*			
7.78 *S* – *D*	7.79 *S*		
8.01 *F* – *D*			

* *S*, strong; *M*, moderate; *F*, faint; *VF*, very faint; and *–D*, diffuse.

† Values by F. J. Williams.

the semihard and hard kaolins more, and the fuller's earth the largest capacity. Base-exchange capacity and the viscosity behavior did not change consistently with grain size, although sedimentation tests show a finer average grain size with "hardness." Electrodialysis emphasizes the possibility of the presence of positive or amphoteric components in some semihard and hard kaolins, inasmuch as deposits on the negative electrode revealed a material of high silica-alumina ratio, with low index of refraction; soluble alumina was also present according to the morin test. The base-exchange capacity at pH 8 of soft kaolins is nearly coincident with a minimum viscosity, whereas the base-exchange capacity of some semihard and hard clays is reached when the clay slip is in a highly viscous condition. The viscosity behavior, therefore, seems to indicate particularly the presence of organic material or minerals other than kaolinite in all of the semihard and hard kaolins.

(4) Microscopic evidence indicates that the kaolins ire composed principally of kaolinite and that authiaenic development of coarse kaolinite crystals has gaken place in all of the kaolins but to a greater extent tn the soft clays. The development of an intermediate stage of crystallization from amorphous or cryptocrystalline material is seen by the presence of

TABLE III

COMPARISON OF CRITICAL *d* VALUES OF CLAYS TESTED WITH PUBLISHED DATA

Clay	*L* value (cm.)	*d* value (a.u.)	Ross and Kerr *d* value (a.u.)
L	1.67	5.29	
Kaolinite*			4.464
Halloysite*			4.42
F, Zettlitz kaolin	2.07	4.294	
Mo. halloysite	2.09	4.238	
Pa. halloysite	2.10	4.318	
Kaolinite*			4.194
B	2.10	4.047	
M	2.22	3.997	
Halloysite*			3.97
A	2.24	3.960	
L	2.28	3.692	
Kaolinite*			3.874
Halloysite*			3.63
Kaolinite*			3.614
Mo. halloysite*	2.49	3.560	
M	2.51	3.535	
Pa. halloysite	2.53	3.512	
F, Zettlitz kaolin	2.54	3.498	
B	2.55	3.485	
Kaolinite*			3.424
A	2.59	3.422	
Mo. halloysite		3.248	

* Clay minerals tested by Ross and Kerr (see footnote 4).

many aggregates with crystal outline and of lower index of refraction than kaolinite. This material had many of the properties of halloysite although it was not definitely identified as such. Further reasons for suspecting the presence of halloysite are found in statements by Ross and Kerr[4] that halloysite tends to be richer in alumina than kaolinite (a relationship found in the analyses of these kaolins; see section VI (2) of Part I, p. 113). They also found in certain kaolin deposits in which halloysite is associated that the relations of the two minerals indicate that the first mineral to form is commonly halloysite and that kaolinite is the result of its recrystallization.[5] Although the most pronounced evidence of this intermediate stage was found in clay F, much disseminated aggregate material was present in all of the kaolins tested. X-ray analyses may be interpreted to show the presence of kaolinite or halloysite or both. Thermal analyses indicate the possible presence of allophane in considerable amount in clay F and of a small amount of allophane or halloysite or both in all of the kaolins.

VI. General Conclusions

On the basis of the evidence, kaolinite is shown to be the principal constituent of a series of Georgia kaolins which are believed to be typical of commercial clays mined along the Georgia Fall Line. The hardness of a kaolin as determined by the producers is shown to be directly related to particle size, that is, the finer the grain size, the harder the clay. If, however, hardness is assumed to include erratic colloidal behavior, factors other than grain size may then be important because the admixture of other minerals and the presence of organic matter greatly affect viscous properties. Two kinds of hard kaolin seem to be recognized; those which are hard only because of fineness of grain and those which are hard because of the presence of organic matter or clay minerals of high base-exchange capacity.

The outstanding difference between the hard and soft kaolins, however, seems to be in the degree of development of kaolinite, the soft clays showing a greater crystallization than the hard clays. Some kaolinite appears to result from the reorganization of a less stable aggregate material having some of the properties of poorly organized kaolinite and some of those of halloysite. Other crystalline particles of kaolinite may have formed at the source during weathering and may have withstood subsequent transportation and deposition.

Author Note

Since the completion of the work presented here, evidence has been obtained from electron microscope photographs of Georgia kaolins which indicates that the material described as being in an intermediate state of development does not have the fibrous characteristics of halloysite but should more properly be classified as a poorly oriented kaolinite. Methods of clay mineral determination other than by the electron microscope fail to bring out this distinction.

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[5] In this connection, note that L. T. Alexander, G. T. Faust, S. B. Hendricks, H. Insley, and H. F. McMurdie, in "Relationships of the Clay Minerals Halloysite and Endellite," *Amer. Mineralogist*, **28** [1] 1–18 (1943), published since this paper was written, conclude that halloysite is a kaolin-type mineral which usually has considerable disorder in the stacking of the silicate layers. They report (in examining weathered rocks from Rockdale, Baltimore County, Md.) that the presence of characteristic "worms" of kaolinite in a base of endellite and halloysite suggests that kaolinite may have been formed by reorganization of the halloysite, which, in turn, was the product of partial dehydration of the endellite.

REHYDRATION STUDY OF CLAYS*

By Louis H. Berkelhamer†

Abstract

The rehydration characteristics of a group of twenty clays were studied by dehydrating at 300°C. and then rehydrating by exposure to a water-saturated atmosphere at 30°C. for periods extending from approximately 28 to 80 days. A sharp differentiation was obtained between the montmorillonite and the kaolinite-illite types of clays.

A simple, rapid rehydration-dehydration test and the results on ninety-five clay samples are presented as an aid in the evaluation of clays. The test can be completed within five hours and permits a limited but useful classification of clays.

I. Introduction

The purpose of this study was to develop a simple method to be used in the evaluation of clays. The unreliability of the benzidine color reaction as a test for montmorillonite[1] prompted this work. A proposed rehydration-dehydration test is offered as an aid in classifying clay types.

(1) Literature Review

Although the literature on the clay minerals is quite voluminous,[2] Grim[2(a)] has pointed out that clays are generally composed of a member or members of the kaolinite, illite, and montmorillonite clay-mineral groups.

Garrison,[3] in an excellent discussion of the surface chemistry of clays and shales, cites the work of Kelley, Jenny, and Brown.[4] They show that minerals retain water in three different ways, namely, crystal water, broken-bond water, and planar water. Crystal water is that water combined into crystal structure, being firmly bound and, in the case of kaolinite, requiring a temperature of about 500°C. to be released. Broken-bond and planar water constitute the attached water, which may be driven off below 350° to 400°C. and which is usually combined at the surface of the sheets and framework that make up the mineral. This water is referred to as adsorbed water. The nature of the surface to which the water is attached determines the strength of bonding, the amount of water bound, and the temperature at which the water may be driven off. The broken-bond water is that portion attached at the broken areas, edges, rims, and ends of the mineral structures. Fine grinding generally increases broken-bond water, and the temperature required to remove this water is more than 200° higher than its normal boiling point. Planar water is that water which is not rigidly attached; it is held by weak electrostatic forces along the tops or bottoms of the flat plates or sheets of the micaceous-like clay minerals and it may evaporate almost as readily as free water.

The water lost during dehydration is generally referred to as "reversibly held." Nagelschmidt[2(b)] states that the reversibly held or adsorbed water of the clay minerals is usually lost below 400°C. and the lattice hydroxyl between 400° and 600°C. (Fig. 1 is taken from Nagelschmidt). He suggests that, from dehydration curves of clays, large losses of water below 400°C. may be due to a mineral of the montmorillonite group and that large losses between 400° and 600°C. may indicate the presence of halloysite or kaolinite.

Hüttig and Herrmann[5] give the same limits for kaolin dehydration as does Nagelschmidt, but they add that calcination at 300°C. gives kaolin its greatest adsorptive power toward methyl alcohol vapor.

Grim[6] shows that illite loses water from its lattice at about 350° to 600°C.; he also indicates that the final destruction of the montmorillonite lattice begins at about 600°C., immediately after the loss of lattice water at about 500°C.

Schwarz[7] describes clays and fuller's earths as having

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This report represents the results of cooperative work between the Bureau of Mines, Department of the Interior, and the University of Alabama.

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[1] J. B. Page, "Unreliability of Benzidine Color Reaction as Test for Montmorillonite," *Soil Sci.*, **51** [2] 133–40 (1941).

[2] (*a*) R. E. Grim, "Relation of Composition to Properties of Clays," *Jour. Amer. Ceram. Soc.*, **22** [5] 141–51 (1939).

(*b*) G. Nagelschmidt, "Identification of Minerals in Soil Colloids," *Jour. Agr. Sci.*, **29**, 477–501 (1939); *Ceram. Abs.*, **19** [7] 172 (1940).

(*c*) S. B. Hendricks and L. T. Alexander, "Minerals Present in Soil Colloids: I, Descriptions and Methods for Identification," *Soil Sci.*, **48** [3] 257–71 (1939); *Ceram. Abs.*, **19** [7] 173 (1940).

(*d*) P. F. Kerr, "Decade of Research on Nature of Clay," *Jour. Amer. Ceram. Soc.*, **21** [8] 267–86 (1938).

(*e*) R. E. Grim and R. H. Bray, "Mineral Constitution of Ceramic Clays," *ibid.*, **19** [11] 307–15 (1936).

[3] A. D. Garrison, "Surface Chemistry of Clays and Shales," *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No. 1027; *Petroleum Tech.*, **2** [1] 14 pp. (1939); *Mining Tech.*, **3** [2] (1939); *Ceram. Abs.*, **18** [6] 165 (1939).

[4] W. P. Kelley, H. Jenny, and S. M. Brown, "Hydration of Minerals and Soil Colloids in Relation to Crystal Structure," *Soil Sci.*, **41** [4] 259–74 (1936); *Ceram. Abs.*, **15** [9] 285 (1936).

[5] G. F. Hüttig and E. Herrmann, "Increase of Solubility of Alumina Contained in Kaolin Due to Preheating Different Gases," *Z. Elektrochem.*, **47** [3] 282–86 (1941); *Ceram. Abs.*, **20** [11] 263 (1941).

[6] R. E. Grim and W. F. Bradley, "Investigation of Effect of Heat on Clay Minerals, Illite and Montmorillonite," *Jour. Amer. Ceram. Soc.*, **23** [8] 242–48 (1940).

[7] F. Schwarz, "Clays and Fuller's Earths: IV, Isobar Dehydration and Absorption of Water of Clays," *Sprechsaal*, **72** [12] 147–48 (1939); *Ceram. Abs.*, **18** [10] 278 (1939).

the property of reabsorbing water at room temperature after they are dried at higher temperatures. He states that reabsorption is most complete and rapid after dehydration temperatures of 160° to 300°C. but is very small above 700°C.

Schachtschabel[8] discusses rehydration and dehydration of kaolin and presents data to indicate that kaolin calcined at 400° to 800°C. can be rehydrated when it is heated in water.

Saxe and Buckner[9] heated several clays at 110°C. for 24 hours and allowed them to stand at room conditions for 24 hours; the various clays tested showed varying degrees of moisture absorption.

Keppeler[10] exposed dry clay samples to the water vapor over a 10% solution of sulfuric acid and noted moisture absorptions of approximately 3 to 11%.

Hendricks, Nelson, and Alexander[11] studied the water-sorption properties of montmorillonites saturated with various cations. They exposed previously dried samples (over P_2O_5 to constant weight) to water vapor at 30°C. and at various relative humidities for a week or longer. At a relative humidity of 90%, the samples achieved an absorption of 18 to 46%, depending on the cation with which the montmorillonite was saturated.

Parmelee and Fréchette[12] have reviewed briefly the studies of other investigators.

(2) Rehydration Studies

Based on the assumption that clay minerals will regain water, or rehydrate, approximately in direct proportion to their losses of reversible water below 300°C., rehydration tests were made in an effort to classify clays.

As a check and also to help distinguish between clays that had similar rehydration properties, a dehydration value at 300° to 600°C. was also determined. This range, as indicated by the literature and by Fig. 1, for the most part covers the breakdown and loss of crystal-lattice water.

II. Method of Investigation

All samples were ground by hand with agate mortar and pestle to pass 100-mesh. Kelley, Jenny, and Brown[4] have pointed out that finer grinding tends to cause crystal-lattice water to be released at temperatures lower than normally expected, which contributes to excessive adsorbed water content. A breakdown of crystal-lattice water is to be avoided for rehydration work and would necessarily interfere with accurate dehydration values over the range of 300° to 600°C.

A group of twenty clays was selected for a preliminary rehydration study at slightly above room temperature; 2 to 4 gm. of minus 100-mesh samples were placed in properly tared, small, ground-glass stoppered bottles (narrow-mouth, 25-cc. capacity). These bottles were placed, unstoppered, in an electric oven at 300°C. for 15 hours or more to obtain constant weight. Rehydration was then carried out by placing the unstoppered bottles in rehydrators (desiccators with water replacing the normal desiccant), which were kept in a thermostatically controlled hotbox at 30°C. At varying intervals, the bottles were removed, stoppered, placed in desiccators, and then weighed for gain in weight through water adsorption or rehydration; this gain was recorded as percentage of the sample weight dried at 300°C. After the rehydration that had occurred during any time interval had been recorded, the unstoppered bottles were replaced in the water-saturated atmosphere of the rehydrators to study the effect of further rehydration. Condensate on the bottles was considered to have an equal effect on all samples, although the only time it was ever noticed was at the end of the study. The appearance of condensate at this time undoubtedly was caused by the saturated condition of the clays.

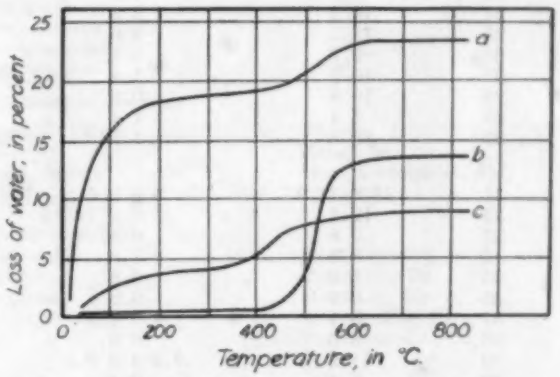

FIG. 1.—Dehydration curves by the intermittent heating method from Nagelschmidt[3(b)]; (*a*) montmorillonite, calcium-saturated supercentrifuged bentonite; (*b*) kaolinite, data from Ross and Kerr; (*c*) illite, data from Grim, Bray, and Bradley.

(1) Rapid Rehydration Test

A rapid rehydration test was developed to allow rehydration properties to be determined in a relatively short time interval. This test consisted of the same procedure described, except that the dehydration period at 300°C. was only 2 hours, followed by a single 2-hour rehydration period at 65°C. Two hours at 300°C. were necessary and sufficient to remove practically all of the water lost at 300°C., and two hours of rehydration at 65°C. gave an appreciable and yet differential water regain without excessive condensation. The same type of rehydrator was used in this test except that the usual cover was replaced by a large watch glass so as not to give an airtight seal and at the same time allow con-

[8] P. Schachtschabel, "Über Dehydratisierung und Rehydratisierung des Kaolins" (Dehydration and Rehydration of Kaolins), *Chem. Erde*, **4** [3] 395–419 (1930); *Ceram. Abs.*, **10** [7] 524 (1931).

[9] C. W. Saxe and O. S. Buckner, "Bonding Strengths of a Number of Clays Between Normal Temperatures and Red Heat," *Jour. Amer. Ceram. Soc.*, **1** [2] 113–33 (1918).

[10] Gustav Keppeler, Berichte der Technischwissenschaftlichen Abteilung des Verbanden keramischer Gewerke in Deutschland, p. 18 (1913).

[11] S. B. Hendricks, R. A. Nelson, and L. T. Alexander, "Hydration Mechanism of the Clay Mineral Montmorillonite Saturated with Various Cations," *Jour. Amer. Chem. Soc.*, **62** [6] 1457–64 (1940); *Ceram. Abs.*, **19** [11] 265 (1940).

[12] C. W. Parmelee and V. D. Fréchette, "Heat-of-Wetting Values of Unfired and Fired Clays," *Jour. Amer. Ceram. Soc.*, **25** [4] 108–12 (1942).

TABLE I

RESULTS OF RAPID REHYDRATION-DEHYDRATION TESTS

Sample No.	Dehydration (% loss at 300°–600°C.)	Rehydration (% gain at 65°C.)	Name	Location
			Kaolin	
1	12.7	0.2	Soft	Washington Co., Ga.
2	12.9–13.0	0.1	"	Wilkinson Co., Ga.
3	11.2	0.3	Hard	Gordon, Ga.
4	11.7	2.1	Soft	Twiggs Co., Ga.
5	10.3	7.6–6.2	Hard	McIntyre, Ga.
6	9.7	3.6–4.5–3.1	Gibson hard	Bessemer, Ala.
7	11.4	1.3–2.5–1.1–2.9	No designation	Gordon, Ga.
8	11.7	0.5	Hard*	Perry Co., Ga.
9	12.4	1.0	No designation*	Alabama
10	12.1	0.7	" "	Florida
11	11.9	0.4	" "	North Carolina
			China clay	
12	11.4	0.3	No designation*	England
13	10.7	0.6	No. 30	"
			Kaolin	
14	11.7–11.4	3.9	Kamec	North Carolina
15	11.3–11.0	1.1	Miller	" "
16	12.5	0.4	Peerless No. 1	South Carolina
17	8.3–8.3	0.1	Pennwood	Pennsylvania
			Clays (ball)	
18	11.3	2.3	No. 90	England
19	7.4–7.6	1.1	No. 5	Kentucky
20	9.9–9.9	3.7	CC	Tennessee
21	7.3–7.0	3.7	Bedminster	England
22	11.0	1.5	Churchill	"
23	9.2	1.0	No. 5	Tennessee
24	14.3	3.3	No. 12	Kentucky
25	12.7	3.6	No. 12*	"
26	9.7	5.5–6.2	KT ivory	"
27	10.7	1.4	No. 1 SGP	Tennessee
28	10.8	0.8	No. 7	"
29	7.4	1.4	No designation*	Mississippi
30	8.5	1.1	Jernigan*	Tennessee
			Clays (miscellaneous)	
31	11.8–11.9	0.8–0.6	Flint	Kentucky
32	12.1	3.9	"	Missouri
33	9.8	0.8	Flint*	Georgia
34	8.9	1.8	Fire (Empire)*	Missouri
35	6.6	0.8	Fire*	Cordova, Ala.
36	6.3	0.8	Bond (Paris brown plastic)	Tennessee
37	8.1	4.8–4.7	Bond or sagger (M&D)	Mississippi
38	6.6	0.6	Sagger Jernigan Special	Tennessee
39	11.8	2.9–4.3–2.5	Sagger Ky. Standard	Kentucky
40	6.1	0.4	Wad (tan)*	Tennessee
41	4.6	0.7	Stoneware	"
42	4.0	0.9	Stoneware*	Alabama
43	3.6	2.3	River*	Tennessee
44	5.1	0.5	Surface	Perth Amboy, N. J.
45	3.6	2.0	"	Alabama
46	2.1	0.6	Brick	Binghamton, N. Y.
47	4.9	1.6	Shale	Bessemer, Ala.
48	3.6	2.3	"	Ottawa, Ill.
49	3.7	0.5	"	Alabama
50	4.5	1.7	"	Kilgore, Ala.
51	3.6	2.2	"	Graysville, Tenn.
			Bentonite	
52	4.7–4.7	15.5	No designation	Hatchechubbee, Ala.
53	4.5–5.5	17.4	" "	Thomasville, Ala.
54	3.5–2.8	21.0–18.6	300 Volclay	Wyoming
55	2.6–2.6	16.4–15.5	Panther Creek	Mississippi
56	4.5	20.8–16.3–14.6	No designation	Near Little Rock, Ark.
57	3.7	17.1–20.6	" "	Laurel, Miss.
58	3.0	12.5	White Pontian	Italy
59	2.9–3.1	11.0	Bleaching clay	Twiggs Co., Ga.

*Where more than one value is given, check tests were run. Samples marked with an asterisk (*) were tested by another operator.

TABLE I (*concluded*)

RESULTS OF RAPID REHYDRATION–DEHYDRATION TESTS

Sample No.	Dehydration (% loss at 300°–600°C.)	Rehydration (% gain at 65°C.)	Name	Location
			Fuller's earth	
60	3.2	23.9–17.2–11.1	Attapulgus	Decatur Co., Ga.
61	2.7	17.2	Off. Oil Chem. Assn.	
62	5.0	24.7	AA	Attapulgus, Ga.
63	5.3	25.9	Q1771	Quincy, Fla.
64	5.5	27.2	Q1772	" "
65	3.2	15.5	H	Macon, Ga.
66	3.1	17.2	L	" "
67	4.6	13.6	No designation	Nocogdoches, Tex.
68	3.9	14.3–9.3–12.8	Exact	Houston, Tex.
69	5.0	22.4	A	Attapulgus, Ga.
			Halloysite	
70	11.9	7.3–6.6–8.5	No designation	Near Bedford, Ind.
71	13.1	4.7	White	Near Rome, Ga.
72	12.7	6.5	Brown	" " "
73	12.8	8.2–9.6	No designation	Brazos Co., Tex.
			Diaspore	
74	12.6–12.7	0.3–1.4	Diaspore	Missouri
			Bauxites	
75	9.8	6.5	Bauxitic clay*	
76	8.2–8.1	10.7–10.7	Morgan	
77	8.3–8.2	10.9	Plastic colloidal	Salina Co., Ark.
78	7.5	13.9	Oolites	Arkansas
79	7.3	16.7	High-grade ore	"
80	8.6	9.5	Low-grade ore	"
81	6.8	10.9	Concentrates	"
82	10.9	9.3	Low-grade ore	"
83	8.0	13.4	Concentrates	"
84	7.1	9.5	Low-grade ore	"
85	7.4	10.3	Concentrates	"
			Miscellaneous types	
86	5.0	0.6–0.5	Phosphate Rock	Florida
87	2.6	0.3	Chalk	Arkansas
88	4.2	0.7	Chalk (Selma)	Near Livingston, Ala.
89	0.2	1.0	Tripoli	Arkansas
90	0.05	0.1	Potter's flint	
91	2.9	0.3	Albany slip clay	
92	4.2	24.7–19.8	Nontronite	Sandy Spring, N. C.
93	10.4	0.1	Dickite	Pottsville, Pa.
94	9.3	16.0	Allophane	Hart Co., Ky.
95	4.1	8.0–7.5	Illite (purified)	Grundy Co., Ill.
95 (*a*)	4.4	14.0–14.5	" "	Vermilion Co., Ill.

Source of Clay Samples Tested (See Table I)

Where no source is given, samples obtained at location or received from individuals: see Nos. 8, 42, 52, 53, 56–62, 69–72, 75, 77–91. All other samples were supplied as follows: Alabama Brick & Tile Co., Nos. 43, 45; American Ball Clay Co., No. 29; American Colloid Co., Nos. 54, 55; Bennett-Clark Co., No. 67; Geo. Bentley, No. 5; Binghamton Brick Co., No. 46; Edgar Plastic Kaolin Co., Nos. 1, 2, 10; Exact Products Co., No. 68; W. S. Dickey Clay Mfg. Co., Nos. 50, 51; Floridin Co., Nos. 63, 64; General Reduction Co., Nos. 65, 66; Georgia Kaolin Co., No. 4; A. P. Green Fire Brick Co., Nos. 32, 34, 74; R. E. Grim, Nos. 95, 95 (*a*); Hammond & Gillespie Clay Co., No. 12; Harbison-Walker Refractories Co., Nos. 6, 7, 33; Harris Clay Co., No. 11; Ironton Fire Brick Co., No. 31; Kaolin, Inc., No. 14; Kentucky Clay Mining Co., No. 19; Kentucky-Tennessee Clay Co., Nos. 23–28, 37, 39; National Fireproofing Corp., Nos. 44, 47, 48; Paper Makers' Importing Co., Nos. 13, 18; C. S. Ross, Nos. 73, 92–94; W. S. Ryle, No. 3; H. C. Spinks Clay Co., Nos. 20, 30, 36, 38, 40; Stephenson Brick Co., No. 35; Thomas Alabama Kaolin Co., No. 9; United Clay Mines Corp., Nos. 15, 17, 21, 22, 76; R. T. Vanderbilt Co., No. 16; Watkins Brick Co., No. 49; West Tennessee Clay Co., No. 41.

FIG. 2.—Rehydrator.

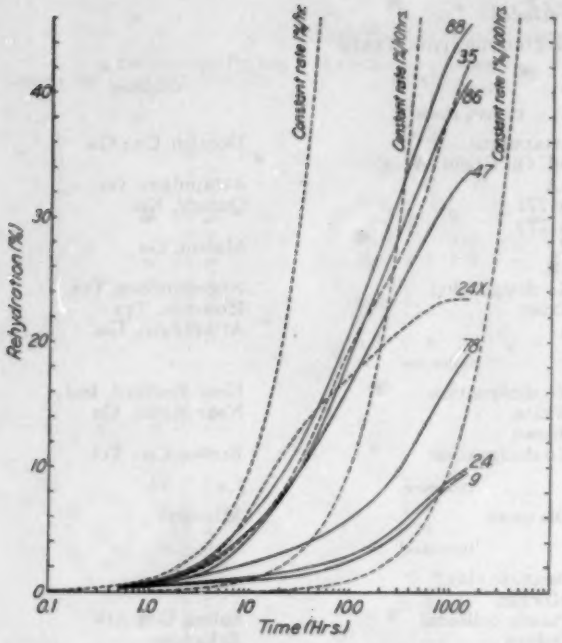

FIG. 3.—Rehydration curves of various clays exposed to water-saturated atmosphere at 30°C.; *curves:* 88, montmorillonite, Thomasville, Ala.; 35, bentonite, Wyo. (Amer. Colloid Co.); 86, bentonite, near Little Rock, Ark.; 47, bentonite, Laurel, Miss.; 24X, halloysite, near Bedford, Ind.; 78, kaolin, Fla. (EPK); 24, china clay, English (PMI); 9, kaolin, Gordon, Ga. (M & M).

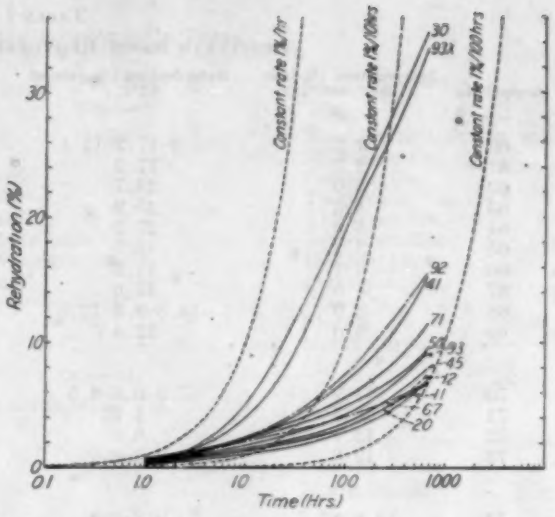

FIG. 4.—Rehydration curves of various clays exposed to water-saturated atmosphere at 30°C.; *curves:* 30, bentonite (Panther Creek), Miss. (Amer. Colloid Co.); 93X, bentonite (300 Volclay), Wyo. (Amer. Colloid Co.); 92, ball clay (Bedminster), English (United Clay Mines); 41, ball clay (CC), Tenn. (H. C. Spinks Clay Co.); 71, kaolin (Kamec), N. C. (Kaolin, Inc.); 50, kaolin (Miller), N. C. (United Clay Mines); 93, ball clay (No. 5), Ky. (Ky. Clay Mining Co.); 45, flint clay, Mo. (A. P. Green Firebrick Co.); 12, surface clay, N. J. (National Fireproofing Corp.); 11, stoneware clay, Tenn. (West Tenn. Clay Co.); 67, shale, Ottawa, Ill. (National Fireproofing Corp.); 20, flint clay, Ky. (Ironton Fire Brick Co.).

densate to collect at the center and drip into a catch funnel as shown in Fig. 2. Chicken-wire screen was used instead of the usual porcelain base-plate designed for desiccators. The rehydrator was kept in a controlled hotbox, and constant conditions were obtained by preheating for approximately two hours before use.

A low-form, wide-mouth, Pyrex-brand sample bottle (5 cm. in diameter by 3 cm. high) with a ground-glass cover gave the most consistent results. The samples weighed approximately 1 gm. each before dehydration treatment. Four bottles were so placed in the rehydrator as not to allow any one bottle to touch another or the desiccator walls as a precaution against condensation. The bottle covers were placed in the hotbox at the same time as the desiccator (keeping the covers at the same temperature as the bottles prevents condensation on the covers which are used later as stoppers). When the bottles were removed from the rehydrator, they were placed on a towel, the visible condensate was wiped from the glass, and the bottles were immediately stoppered with the warm covers. If a drop of condensate visibly wet the sample (as could be seen by the color of the wet spot), the results were not reliable. All weighings after treatment were made on an analytical balance, correct to 0.1 mg.

(2) Dehydration Test

A dehydration check test at 300° to 600°C. was run at the same time as the rapid rehydration test was performed. A duplicate sample was dehydrated at 300°C. for 2 hours with the rehydration sample, weighed, and then returned for 2 hours to the electric oven set at 600°C., with subsequent weighing. The loss in weight on dehydrating at 300° to 600°C. was recorded as percentage of the sample weight dehydrated at 300°C. The type of bottle used for this test did not matter as long as it was of Pyrex-brand glass.

III. Results

(1) Low-Temperature Rehydration

The smooth curves of Figs. 3 and 4 show the results obtained from the preliminary rehydration study at 30°C. of the clays tested (as listed in the legends of the figures). Values of percentage rehydration for a set of eight clays studied in the same rehydrator have been plotted up to 1500 hours of rehydration. (The test, however, was carried to 1960 hours before termination was decided because of erratic results noted during the last approximate 400 hours.) A second set of twelve clays, started later than the first set in another rehydrator, terminated arbitrarily at the same time.

All values have been plotted in Fig. 4, and constant-rate curves have been plotted in Figs. 3 and 4 to help interpret the results. From both sets of curves, except for the one halloysite sample, a distinct grouping of montmorillonite type from other clay types can be easily seen. This grouping was definitely established at the end of 10 hours, and from then on the differentiation became more distinct. During the first 50 hours,

TABLE II

SUMMARY OF RESULTS OF RAPID REHYDRATION-DEHYDRATION TESTS

Clay samples	Range of rehydration (% gain at 65°C.)		Range of dehydration (% loss at 300° to 600°C.)	
	All samples	Majority	All samples	Majority
Kaolins	0.1–7.6	0.1–1	8.3–13.0	11–13
Ball clays	0.8–6.2	1–4	7.0–14.3	7–11
Flint clays Fire clays Bond clays Sagger clays	0.4–4.8	0.5–2	6.1–12.1	6–10
Stoneware clays River clays Surface clays Shales	0.5–2.3	0.5–2.5	2.1–5.1	2–5
Bentonites Bleaching clays Fuller's earths	9.3–27.2	10–20	2.6–5.5	3–5
Halloysites	4.7–9.6	5–8	11.9–13.1	12–13
Diaspore	0.3–1.4		12.6–12.7	
Bauxites	9.3–16.7	9–11	6.8–10.9	7–9
Nonclays	0.3–1.0	0.1–1	0.2–5.0	0.1–5

the halloysite sample acted similarly to the montmorillonites, but it then changed sharply to slow up in rehydration and was the only clay tested to reach apparent saturation at approximately 1000 hours. Some of the ball clays and kaolins tended to show more active rehydration characteristics than the other ball clays and kaolins tested. This reaction no doubt was intimately related to their particle size and exchangeable bases. The shale, surface clay, fire clay, and flint clays seemed to fall fairly close in one group. At the termination of the study, all of the samples except halloysite were still adsorbing water. At the end of 1000 hours, the montmorillonites had adsorbed water to an extent of approximately 32 to 44% of their dry weight at 300°C. Under similar circumstances, the other types of clays except halloysite had water adsorptions that ranged from approximately 7 to 17%. At 1000 hours, the halloysite sample apparently had become saturated with approximately 23.5% of adsorbed water.

(2) Rapid Rehydration-Dehydration Test

Table I gives the results of ninety-five samples tested by the rapid rehydration-dehydration methods. Where more than one value is given, check tests were run. Samples marked with an asterisk (*) were tested by a second operator. Although checks on rehydration were satisfactory, they were not so good as the dehydration values, particularly the montmorillonitic high-rehydrator values, as might be expected. The data of Table I, except for the last group of materials, may be summarized as shown in Table II.

The montmorillonitic clays (bentonite, bleaching clay, and fuller's earth) are readily separated from the others by virtue of a high to extremely high rehydration value accompanying a medium-low dehydration value. Except for diaspore, the purely kaolinitic clays (kaolins) may be distinguished by their extremely low rehydration and high dehydration. The kaolinitic-illitic clays, making up the ball-clay group as well as the flint-, fire-, bond-, and sagger-clay group, each have low rehydration and medium-high dehydration values. The highly illitic shale-, surface-, river-, and stoneware clay group is characterized by low rehydration and medium-low dehydration. The values for nonclay materials are similar to those for the highly illitic clays, but a rough plasticity test (if appearances are deceiving) will quickly distinguish between the two groups. Halloysites are identified by a medium-high rehydration and a high dehydration value, whereas bauxites are roughly the reverse.

TABLE III

EFFECT OF NONCLAY IMPURITY ON RAPID REHYDRATION-DEHYDRATION TEST*

Sample or mixture	Rehydration (% gain at 65°C.)	Dehydration (% loss at 300°–600°C.)
Illite	14.2	4.4
60 illite—40 potter's flint	7.3	2.7
30 illite—70 potter's flint	0.8	1.4
Potter's flint	0.1	0.05

* Similar data were obtained for kaolinite and montmorillonite.

IV. Discussion

The results of the long-period rehydration tests at 30°C. agree with dehydration data reported in the literature. Dehydration at 300°C. apparently does not destroy the hydration properties of the clays tested but merely removes the reversible water which is readily regained when the clays are exposed to a moisture-laden atmosphere. Indirect proof of this action is the rehydration that occurs according to what was expected from the known mineralogical composition and properties of the clays.

The rapid rehydration-dehydration tests have yielded data which roughly classify the clays. That such values are characteristic of a clay's composition (clay minerals plus impurities) and not merely of the clay

mineral present is shown by the additional data of Table III. The values for the purified illites given in Table I are for a 0.1- to 0.06-micron fraction of relatively pure illite clay mineral. The extremely fine size is one factor that contributes to the high rehydration of these illites as compared to the highly illitic clays (shales, surface clays, etc.). Table III, however, shows the effect of the impurity factor, such as an appreciable amount of quartz found in natural shales. A nonclay impurity, such as quartz, acts as a diluent.

The rehydration of kaolinite is well represented by the kaolins, which are essentially composed of this clay mineral. The amount of variation in rehydration is small. The ball-clay group and the flint-, fire-, bond-, and sagger-clay group exemplify the impurity factor when there is present more than one clay mineral (in addition to nonclays) as well as an appreciable amount of exchangeable bases.

The rehydration of montmorillonite covers quite a wide range, shown by the test values for the bentonite, bleaching-clay, fuller's-earth group. This range of rehydration undoubtedly is the result of the extreme variations in base-exchange properties exhibited by the montmorillonite clay minerals.

The sample of allophane tested, in contrast to halloysite with which it is generally associated, gave a high rehydration value comparable with that for a montmorillonite. It differed from the latter, however, in having a high dehydration value.

A nontronite sample showed rehydration-dehydration properties of the montmorillonite group of clay minerals, of which it is properly a member. A sample of dickite gave values similar to those for kaolinite.

Although the rapid rehydration test at 65°C. classifies a clay as a kaolinitic-illitic, halloysite, or montmorillonite type, the accompanying rapid dehydration test (300° to 600°C.) is necessary to pick out the pure kaolinites. The test also helps to separate roughly the highly illitic from the kaolinitic-illitic clays. Finally, because of its accuracy of determination, the dehydration test serves as an excellent check on the rehydration test.

V. Summary

The rehydration properties of twenty different clays were studied at 30°C. in a water-saturated atmosphere after first dehydrating at 300°C. to constant weight. A grouping of the montmorillonite type distinct from that of the other clay types was found. A halloysite that was tested acted similarly to the montmorillonites in rehydration, but this similarity occurred only for the first 50 hours; rehydration slowed after that and the sample apparently became saturated at about 1000 hours. All other test clays were still adsorbing water when the study was terminated, after a period exceeding 1500 hours in some instances.

A rapid rehydration (65°C.)-dehydration (300° to 600°C.) test has been developed (duplicate samples subjected to 2 hours' dehydration at 300°C., followed by a 2-hour rehydration period of 65°C. for one sample and a 2-hour dehydration period at 600°C. for the other. Ninety-five samples were tested; these samples included kaolins and china clays, ball clays, fire clays, flint clays, bond clays, sagger clays, stoneware clays, river clays, surface clays, shales, bentonites, bleaching clays, fuller's earths, halloysites, illites, bauxites, diaspore, dickite, nontronite, allophane, Albany slip clay, and some nonclays (chalk, tripoli, phosphate rock, and potter's flint).

A classification has been set up, based on the results of this rapid test, affording a quick and simple method of typing clay samples received for evaluation. The test can be completed within five hours, and it is relatively independent of the personal equation.

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AN IMPROVED VOLUMENOMETER*

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Abstract

A volumenometer of improved design has been developed for measuring the solid volumes of specimens varying in size up to that of standard refractory bricks. The chief feature of the new design is the use of a closed-cistern, altitude-type mercurial barometer to replace the simple manometer previously used. The barometer is designed for use in a constant-temperature room (21.1°C.) where the acceleration of gravity is 980.1 cm. per sec.^{2}. Under these conditions, pressure readings are automatically corrected to standard conditions. A vernier permits rapid readings to 0.1 mm. of mercury.

I. Introduction

The gas-expansion method for determining the solid volumes of porous specimens makes use of a gas (usually air) as the absorption fluid. The solid volume of a specimen is measured by the change in pressure which accompanies a known change in the volume of a closed system containing the specimen.

The advantages of the gas-expansion method over the liquid-absorption method for measuring solid volume are as follows: (1) the gas has a low viscosity compared to that of liquid and will enter certain fine pores which liquids do not penetrate; (2) in a very permeable material with large pores, such as some types of insulating refractories, some of the liquid may drain from the specimen before it can be weighed; (3) the gas-expansion method may be applied without harm to materials which would be damaged by a liquid; and (4) any convenient size or shape, including granular material, may be measured by the gas-expansion method.

II. Survey of Literature

The principle of the gas-expansion method was employed by Zehnder[1] as early as 1903 in an effort to perfect a rapid method for determining the true density of a material. Washburn and Bunting,[2] however, appear to be the first to have extended the method to the determination of porosity; in one of their papers,[3] they have described a volumenometer designed to measure the solid volume of a full-sized brick, and this method was further developed by Bole and Jackson,[4] who used an inclined manometer. Pressler[5] used a volumenometer for rapid routine testing of refractory brick. A vertical open-end manometer was used to measure the pressure differences, and the barometric pressure was eliminated from the calculation by cancellation.

All of the foregoing methods called for the use of a vacuum pump to obtain the necessary change in pressure in the apparatus. It remained for MacGee[6] to eliminate the pump. A bulb of known volume was filled with mercury while the brick container was open to the atmosphere; the container was then closed and the calibrated bulb was emptied, thus increasing the volume of the system by an amount equal to the volume of the bulb.

Stull and Johnson[7] designed a volumenometer for use with building brick. The principal improvements over MacGee's design were the use of a millimeter scale engraved on a mirror, by which readings of the manometer were estimated to 0.1 mm.; an adjusting screw on the supporting clamp for the mercury bulb, which facilitated adjusting the height of the mercury at the leveling marks; and a chain counterbalance, which made it easier to raise and lower the mercury bulb.

In designing a new apparatus for determining the solid volumes of larger specimens, up to and including standard refractory brick, the apparatus designed by Stull and Johnson was taken as a point of departure. Their apparatus had been in use at the National Bureau of Standards for more than six years.

The expansion chamber of the Stull and Johnson apparatus is made of cast brass, and it is large enough to take a standard building brick. A lapped joint between the cover and the chamber provides an air-tight seal. The volume of the calibrated bulb is 244 ml. between calibration marks. The manometer is 8-mm. bore tubing, which gives menisci sufficiently flattened so that good check readings may be obtained.

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III. Description of Improved Instrument

The improved apparatus has three essential parts, namely, the barometer used to measure pressures in the closed system, the expansion chamber, which holds the specimen while it is being measured, and the evacuating apparatus.

(1) Barometer

The essential details of the closed-cistern altitude-type mercurial barometer are shown in Fig. 1. With this type of barometer, the level of mercury in the cistern varies inversely with the level of mercury in the tube. The scale on the barometer is constructed to compensate for the change in level in the cistern. In computing the length of a scale division, factors are included which automatically correct readings made at a specific temperature and gravitational constant to the standard conditions of 0°C. and gravity at sea level. The corrections for temperature and gravity, however, are relatively small.

The barometer was designed and constructed for use in a constant-temperature room (21.1°C.) at the National Bureau of Standards, where the acceleration of gravity is 980.1 cm. per sec.[2]. The pressures indicated by the barometer under these conditions were found to agree (within 0.2 mm. of mercury) with pressures determined by means of a standard barometer, corrected to 0°C. and gravity at sea level. A barometer of this type can be designed to correct for any given conditions of temperature and gravity, or a calibration chart may be prepared for use at temperatures other than those for which the instrument is designed.

The barometer tube is 12 mm. in inside diameter, and the cistern has an inside diameter of approximately 75 mm. The length of one division on the scale is approximately 0.976 mm. A vernier is provided to permit rapid readings to 0.1 scale division over the entire scale.

The immersion of the tube below the surface of the mercury in the cistern is considerably more than that in the usual barometer. It is thought that this deeper immersion will delay the leakage of air into the vacuum space. If the vacuum does become impaired, it may be renewed by forcing the bubble of gas through the mercury-sealed check valve at the top of the tube. To do this, the space above the mercury seal is evacuated, and pressure is applied to the mercury in the cistern to cause the mercury to rise in the tube, opening the check valve and carrying the gas bubble through. As the pressure in the cistern is lowered gradually, the check valve closes when there is just enough mercury left in the chamber to float the valve into its seat. If the upper chamber is now opened to the atmosphere, the valve closes tightly to form a permanent seal. It may be advantageous to perform this operation at an elevated temperature in order to eliminate water vapor from the vacuum space.

A filter chamber of liberal dimensions occupies the space immediately below the cistern. Air enters at the bottom of the chamber, passes through the cotton filter material, and then through the holes in the cistern wall to the top of the cistern. Access to the filter chamber for renewal of the filter material is obtained by removing the bottom plate. This plate is sealed by a narrow sulfur-free rubber gasket (see *B*, Fig. 1), which slightly more than fills the groove in which it is placed. When the ring of screws is tightened, the pressure in the rubber is sufficient to make an airtight seal.

FIG. 1.—Schematic drawing of closed-cistern, altitude-type mercurial barometer designed for use with the volumenometer; *A*, ring of screws for sealing cistern; *B*, sulfur-free rubber gasket; and *C*, auxiliary cistern.

Facilities for easily cleaning the cistern have been provided. If the ring of screws at *A* (Fig. 1) are removed, the cistern, together with the filter, may be lowered, leaving the auxiliary cistern, *C*, to hold the mercury in the tube. After the cistern is cleaned and supplied with clean mercury, it is replaced. The top cover plate is sealed with a gasket similar to that at *B*. These gaskets produce a tight seal without the use of a sealing compound, making it possible to open and close the cistern or filter chamber as often as necessary without spoiling the gaskets.

The barometer has been successfully transported in its normal upright position after evacuating and sealing the system so that most of the mercury is in the cistern. The deep immersion of the tube helps to prevent air from leaking into the vacuum space when the mercury in the cistern is disturbed.

(2) Expansion Chamber

The expansion chamber, $4^3/_4$ by $2^3/_4$ by $9^1/_2$ in. inside, is large enough to hold a standard refractory brick. It is constructed of $^3/_8$-in. hot-rolled sheet steel, all joints being brazed. The chamber is mounted with the long dimension vertical to reduce the area of the cover to a minimum. A circular flange, 10 in. in diameter and $^3/_4$ in. thick, is brazed to the top of the chamber. The circular steel cover is $^3/_4$ in. thick and 10 in. in diameter. A needle valve is mounted in the center of the cover so that the system can be opened to the atmosphere without removing the cover. There is a lapped joint between the flange and the cover.

A stirrup, made from $^1/_2$- by $^3/_4$-in. strip steel, is used to place specimens in the chamber and to remove them. Rings on each side of the stirrup form convenient handles, which may be folded down into the chamber before it is closed. The walls are recessed to

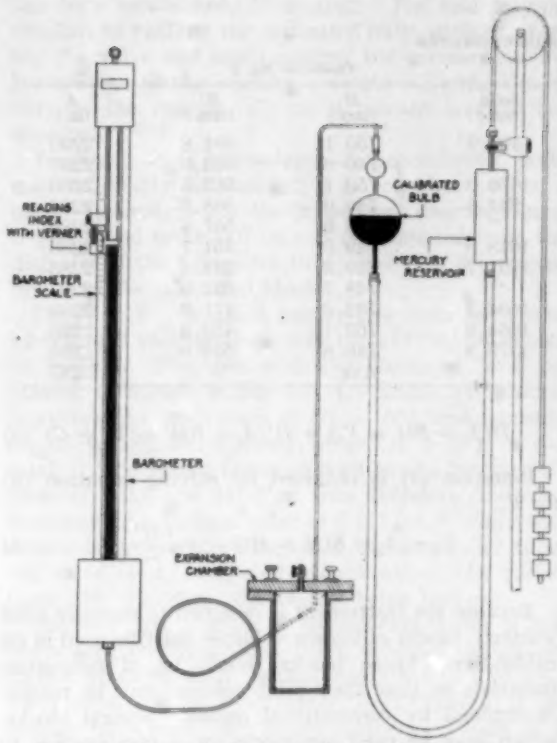

FIG. 2.—Schematic diagram of the volumenometer.

hold the stirrup so that it will not protrude into the chamber.

(3) Evacuating Apparatus

The volume of the closed system is varied with the aid of a glass bulb, which is first filled with the mercury and then emptied. The mercury flows to and from a reservoir attached to the bulb by flexible tubing. The reservoir is raised and lowered by means of a sliding carriage, and a chain counterbalance facilitates this operation. A slow-motion screw aids in bringing the level of the mercury exactly to the calibration marks on the bulb. The volume of the bulb is nominally 500 cc. (507 cc. for this instrument) between calibration marks. A mercury trap above the bulb helps to prevent mercury from overflowing into the expansion chamber.

(4) Assembly

The various parts of the apparatus are mounted on a structural steel framework to form a compact, self-contained unit. A schematic diagram of the assembly is shown in Fig. 2 and a photograph of the complete assembly in Fig. 3. In order to assure a closed system of constant volume, rigid metal tubing is used to connect the various parts of the apparatus. Standard pipe fittings are used throughout, and couplings are conveniently placed so that any part of the assembly may be removed without disturbing the other parts.

The assembled apparatus occupies a floor space of approximately 2 by 2 ft., and it is 6 ft. high. Although some parts are fragile, it may be easily moved from place to place. If it is to be transported for any considerable distance or if it is to be subjected to jarring, the mercury should be removed from the reservoir and the barometer evacuated.

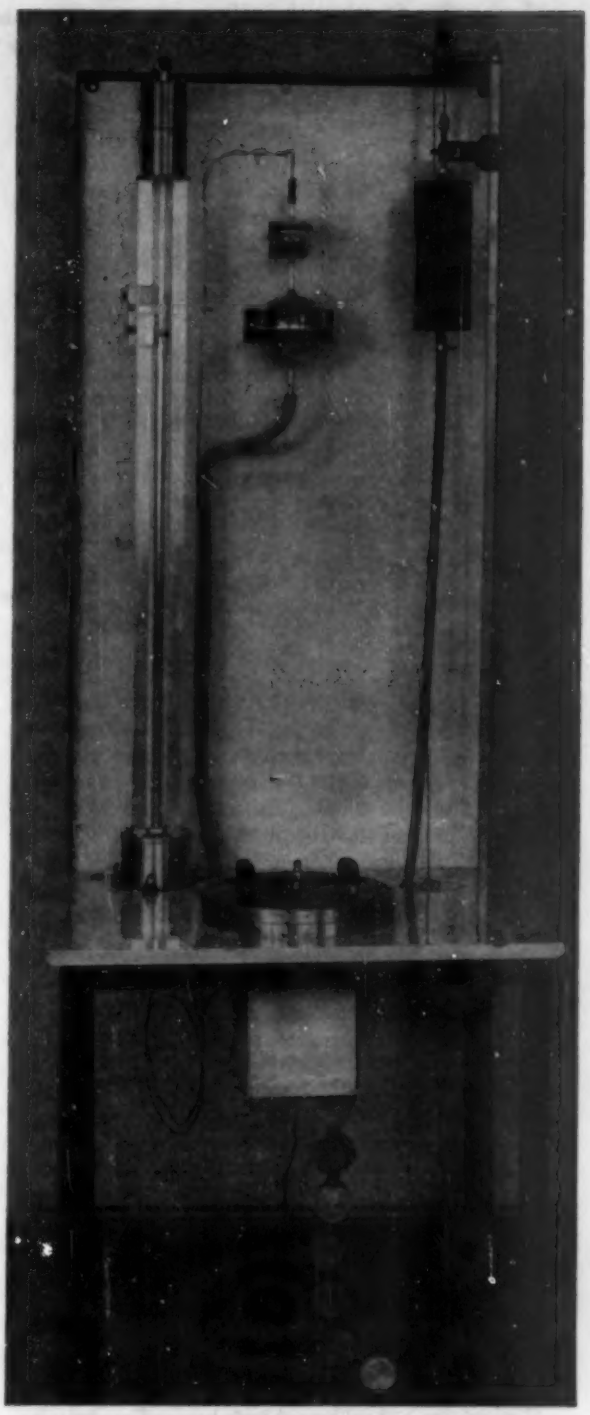

FIG. 3.—Photograph of volumenometer.

TABLE I

CALIBRATION OF VOLUMENOMETER

Operator No. 1			
Solid vol.	H (mm.)	H' (mm.)	A (cc.)
1042.1	752.0	551.5	2292
"	789.7	579.8	2290
"	751.7	551.2	2291
"	728.5	533.8	2292
868.4	752.3	568.7	2292
"	745.5	563.5	2292
"	751.8	568.3	2292
"	782.9	592.2	2289
694.7	751.6	582.4	2293
"	771.7	598.1	2289
"	751.6	582.4	2292
"	743.1	575.6	2290
521.0	753.1	595.8	2291
"	754.6	597.0	2291
"	751.6	594.6	2291
"	736.9	582.9	2293
347.3	750.9	604.9	2297*
"	749.4	603.6	2295*
"	751.7	605.5	2295*
"	751.8	605.6	2296*
173.7	755.2	617.6	2289*
"	752.0	614.9	2291*
Avg.			2291

* Omitted in averaging.

Operator No. 2			
Solid vol.	H (mm.)	H' (mm.)	A (cc.)
496.9	750.1	594.8	2290
"	746.8	592.0	2287
670.6	750.1	582.6	2286
844.3	749.9	568.5	2286
"	748.6	567.4	2286
1018.0	749.6	551.7	2286
1191.7	749.3	531.4	2285
"	748.7	531.0	2287
1604.3	762.9	471.3	2288
1664.9	763.1	456.8	2286
1375.3	746.8	504.9	2295
	Avg.		2287

IV. Calibration of Volumenometer

The volume of gas in the cistern of the barometer varies with the height of the column of mercury in the tube. The volume of gas, V_g, in the closed system, with a specimen of solid volume, V_s, in the chamber, and the calibrated bulb filled with mercury, may be expressed by equation (1).

$$V_g = A + BH - V_s \qquad (1)$$

V_g = gas vol. (cc.) in closed system.
V_s = specimen of solid vol. (cc.) in chamber.
A = gas capacity (cc.) of closed system, with no specimen in chamber, when calibrated bulb is filled with mercury to upper graduation and mercury level in barometer tube is same as that in cistern.*
B = vol. (cc.) of barometer tube per scale division.
H = barometer reading in scale divisions or pressure (mm.) of mercury corrected to standard conditions.

* An extra constant has been combined with A to compensate for the diminished volume of the barometer tube caused by the constriction.

When the mercury is drained from the calibrated bulb to the lower graduation, the gas in the closed system expands to replace it and the barometer reading decreases to H'; the final volume of gas in the closed system, V'_g, is given by equation (2).

$$V'_g = A + BH' - V_s + C \qquad (2)$$

C = vol. (cc.) of calibrated bulb between graduations.

Inasmuch as the product of pressure and volume is constant,

$$H \times V_g = H' \times V'_g$$

By substituting V_g and V'_g from equations (1) and (2), equation (3) follows.

$$H(A + BH - V_s) = H'(A + BH' - V_s + C) \qquad (3)$$

Equation (4) is obtained by solving equation (3) for V_s.

$$V_s = A + B(H + H') - \frac{CH'}{(H - H')} \qquad (4)$$

Because the instrument is designed to measure solid volumes, blocks of known volumes must be used in its calibration. These blocks should be of nonporous materials so that their solid volumes can be readily determined by conventional means. Several blocks, which may be used separately or in combination to cover the working range of the instrument, should be provided. The steel blocks used by Stull and Johnson[7] and other blocks of known volume were employed in this investigation.

The calibrating blocks are customarily allowed to remain overnight in the room with the volumenometer in order to come to room temperature before making determinations. When the blocks are ready, the cover of the expansion chamber is removed and one or more of the blocks are introduced, using the stirrup provided for that purpose. The flanges are wiped clean to remove grit and are lightly greased with petrolatum; too much or too little petrolatum makes it difficult to obtain a good seal. The cover is placed on the chamber with the valve opened and manipulated, like the cover of a desiccator, until a good seal has been obtained. It may help to obtain a good seal if the closed system is partially evacuated before manipulating the cover. This may be done by filling the calibrated bulb with the valve open, closing the valve, and emptying the calibrated bulb. If the change in pressure over a 5-minute period after the chamber has been evacuated does not exceed 0.1 mm. of mercury, the virtual absence of leaks is indicated.

When a satisfactory seal has been obtained, the mercury reservoir is raised, and the level of the mercury in the calibrated bulb is adjusted to the upper graduation, using the slow-motion screw provided for that purpose. With the valve in the cover of the expansion chamber closed, the initial pressure, H, is read on the barometer. The mercury reservoir is then lowered, and the level of mercury in the calibrated bulb is adjusted to the lower graduation. When equilibrium

has been established, H' is read. The seal may be checked by refilling the calibrated bulb, without opening the valve and again reading the pressure on the barometer. If this reading is within 0.1 mm. of mercury of the reading, H, no significant leakage has occurred.

Inasmuch as C, the volume of the calibrated bulb, may be readily determined, it is considered to be a known quantity. For the instrument described here, C was found to be 507 cc.; B is computed from the diameter of the barometer tube; and A is determined by use of the calibrated blocks.

Operator No. 1 made twenty-two tests on blocks having solid volumes from 1042.1 to 173.7 cc., as shown in Table I. The tests with the blocks of 347.3 cc. volume give high values for A. Small test blocks, however, give low values of $(H - H')$, and accurate results cannot be expected when $(H - H')$ is too small.[2] The values obtained with blocks having volumes of 173.7 and 347.3 cc. were therefore discarded in averaging. Using a value of 0.111 for B, which was computed from the diameter of the barometer tube, the value of A, computed from equation (4), varied from 2289 to 2293 cc., the average being 2291 cc.

Operator No. 2 made a second calibration of the instrument one year later, using different calibration blocks, which varied in volume from 496.6 to 1664.9 cc. Each value reported by operator No. 2 (Table I) is the average of at least three determinations. Values of A varied from 2285 to 2295 cc., the average being 2287 cc. The value of 2287 cc. for A seems preferable to 2291 cc., inasmuch as it has been obtained more recently and also on solid volumes in the range to be measured with the instrument.

If the values of A show a systematic variation as V_s is varied, it indicates that the values of B or C may be in error and should be redetermined. In the present investigation, variations in A with V_s were not systematic and were no greater than those in A with V_s constant. Equation (5) is derived from the selected values for A and B of equation (4).

$$V_s = 2287 + 0.111(H + H') - \frac{507H'}{(H - H')} \qquad (5)$$

V. Measuring Solid Volume of Porous Specimen

The solid volume of a porous specimen may be computed from equation (5) if H and H' are known.

The precautions mentioned in section IV under calibration of the instrument, namely, (1) removal of grit from the flanges, (2) allowing the specimens to come to room temperature before starting determinations, and (3) securing a tight seal, are equally important when a porous specimen is measured. To obtain H, the specimen is introduced into the chamber, which is sealed as previously described. The mercury is then adjusted to the upper graduation of the calibrated bulb, and H is read after equilibrium is established. This value of H may or may not be atmospheric pressure. In any event, once the valve has been closed, any change in atmospheric pressure will have no effect on the pressures in the closed system and so cannot affect the accuracy of results. Check determinations may be made if desired with different values of H.

Because the air escapes slowly from fine pores, some brick may require as long as 20 minutes for equilibrium to be established after the mercury is drained from the calibrated bulb. It is safe to assume that equilibrium has been established when the change in pressure over a 5-minute period does not exceed 0.1 mm. of mercury. As soon as this condition has been attained, the mercury is adjusted to the lower graduation of the calibrated bulb and H' is read on the barometer.

It is usually desirable to make two or more check determinations on each specimen. This may be done without removing the specimen from the chamber by raising the mercury reservoir and filling the calibrated bulb without opening the system to the atmosphere, in which case duplicate readings of H and H' should be obtained. If the second value H does not vary from the original H by more than 0.1 mm., it indicates that no significant leakage has occurred. An independent check may be obtained by opening the valve in the cover and starting over again, choosing a different value of H in the second determination. In any case, approximately the same length of time is required for the air to fill the pores of the specimen as was necessary to remove it in the first test.

When small specimens are tested, it is desirable to fill as much as possible of the open space in the chamber with blocks of known volume to increase the precision of the determination.[3]

It is advisable for the operator to start each day's work with a redetermination of the volume of a calibrating block to see that the instrument is working properly. Each time a new specimen is inserted, it should be carefully determined that a tight seal has been obtained.

VI. Advantages of Improved Volumenometer

The description of the instrument has shown that it is portable and self-contained. The chief new feature of the design is the use of a closed-cistern, altitude-type mercurial barometer to measure pressures. This feature eliminates inaccuracies caused by changes in atmospheric pressure during a test, and the use of the instrument in a constant-temperature room eliminates inaccuracies resulting from temperature changes during a test. The barometer is so designed that pressure readings are made directly in millimeters of mercury, corrected to standard conditions.

The vernier on the barometer is a distinct advantage in reading pressures, for it increases the precision of such readings and makes possible accurate readings by an unskilled observer. The auxiliary bulb above the calibrated bulb acts as a trap to prevent mercury from overflowing and relieves the operator from the need for great care in raising the mercury reservoir.

There is apparently no instrument which relieves the operator of the need for considerable care in obtaining a tight seal. The method described for rechecking the H value after a determination has been completed will, however, reveal even a slight leak.

National Bureau of Standards
Washington, D. C.

(1943)

DIRECT RADIANT KILN FIRING IN THE CERAMIC INDUSTRY*

By Harry W. Smith, Jr., and J. A. Ehlinger

Abstract

The method of radiant gas firing without muffles, fire tubes, or in some cases saggers is described.

I. Introduction

A fundamentally new technique of kiln firing is described, which involves the combustion of gaseous fuels "catalytically" on the concave surfaces of a multiplicity of incandescent ceramic cups distributed in pattern over the kiln walls without muffles, baffles, or fire tubes between burning gases and ware. This technique, called "direct radiant gas firing," for full-scale manufacture of ceramic products dates from the initial run through the circular bisque kiln at Lenox, Incorporated, in November, 1940.[1]

No single technique of heat generation or manipulation fits all products or all conditions of production. Direct radiant firing technique, however, has already given satisfactory results in producing first-grade china bisque; steatite bodies; single-fired electrical, mechanical, and novelty porcelains; close-tolerance, high-temperature refractory shapes; and certain glazes. In other branches of ceramic firing, such as decoration and porcelain enameling, laboratory trials of direct radiant gas firing have been made, but none of these has been on a production scale. The extent to which direct radiant gas firing can improve production practice may be determined only after cooperative development and actual operation of pilot plants on the customer's premises.

II. Basic Principles

Those features which make direct radiant gas firing fundamentally different from other combustion methods are shown in Fig. 1. Premixed gas and air in appropriate ratio (and under pressures of a few inches of water column up to 3 lb. per sq. in.) is delivered centrally to the base of a cuplike concavity in the burner block. A close-tolerance ceramic tip is slotted around its periphery at this point to distribute the fuel among many small component flames, each directed so that it sweeps the surface of the burner concavity radially from the center toward the rim. The surface of the cup thus becomes more or less uniformly incandescent with the following important results:

(1) The rate of combination of gas and air is accelerated by "surface" or "catalytic" combustion in scrubbing contact with highly incandescent refractories, and the combustion reaction is therefore carried to its end point entirely within the cup and at a gas temperature above 2200° or 2300°F. Researches have shown that if combusting gases are chilled below 2200°F. at any time during the interaction, "complete combustion" cannot be attained.

Fig. 1.—Features of direct radiant gas firing.

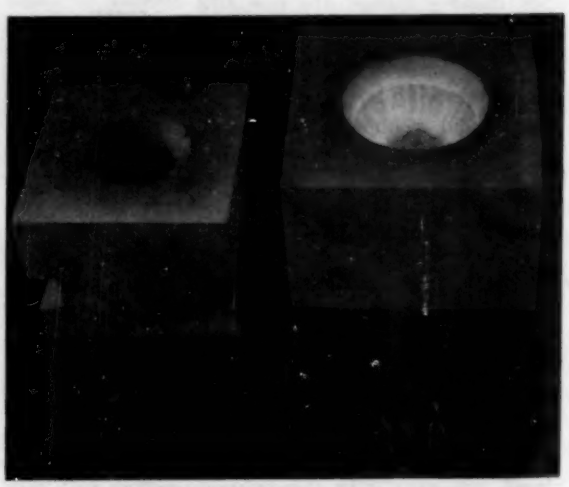

Fig. 2.—Underexposed photograph to show distribution of incandescence.

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 23, 1942 (Materials and Equipment Division). Received August 21, 1942.

[1] F. O. Hess and Leslie Brown, "Perfect Firing of Fine Chinaware in Radiant-Heat Kiln," *Ceram. Ind.*, **36** [6] 55, 58–59 (1941); *Ceram. Abs.*, **21** [4] 88 (1942).

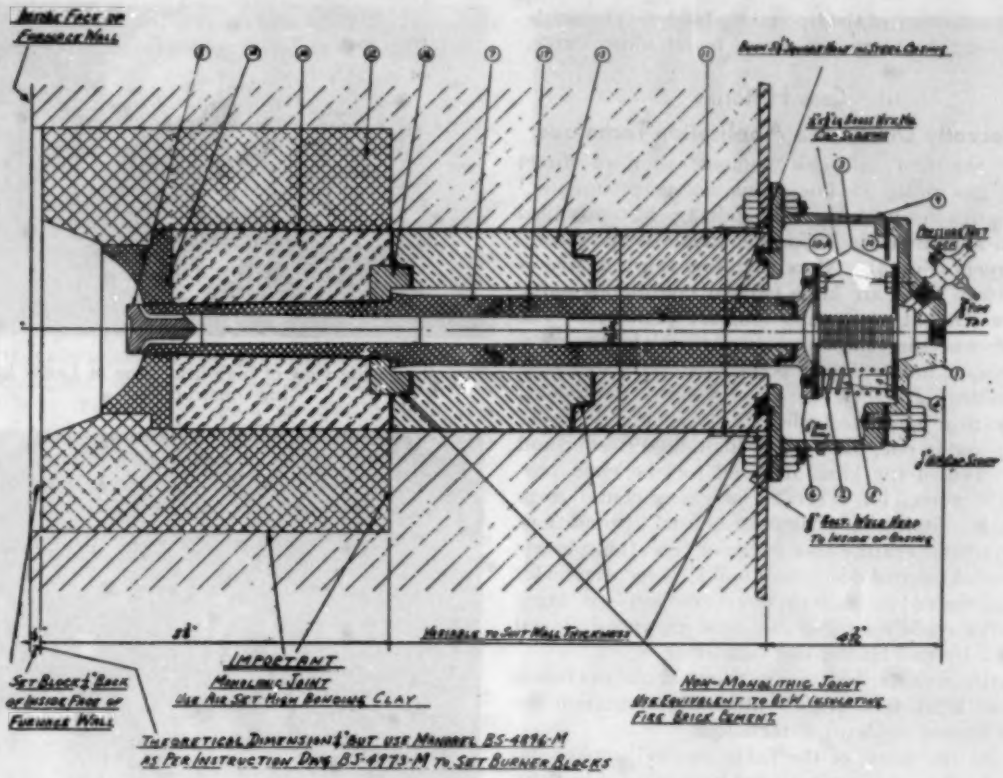
IMPORTANT
MONOLITHIC JOINT
USE AIR SET HIGH BONDING CLAY
NON-MONOLITHIC JOINT
USE EQUIVALENT TO B&W INSULATING FIRE BRICK CEMENT
SET BLOCK 4" BACK OF INSIDE FACE OF FURNACE WALL
THEORETICAL DIMENSION 4" BUT USE NUMBER BS-4896-M AS PER INSTRUCTION DWG BS-4973-M TO SET BURNER BLOCKS

FIG. 3.—Cross section of assembly of radiant gas burner.

(2) The high degree of incandescence attained on the cup surface (about 2850°F. in the usual burner designs and possibly higher in more recent designs) produces a substantial quantity of radiant heat in addition to the convected heat always associated with gas-air combustion. As a result of this heat inherent in the fuel, which is liberated in radiant form, less heat is delivered in convected form, exhaust gas temperatures can be lowered, and kiln thermal efficiencies are increased. Because of the contour and appreciable surface area (usually about 20 to 25 sq. in.) of the incandescent refractory, the radiation is also showered evenly over a considerable area, depending on the distance between the burner and the ware.

(3) The considerable temperature difference, called "radiant head," between the radiating source (the burner cup) and the receiver of radiation (the ware) results in an extremely rapid rate of heat transfer, according to the Stefan-Boltzmann law of the "difference between the fourth powers of the absolute temperatures."

(4) The products of combustion curl back from the rim of the cup toward its base. The stream velocities of the combustion products are thus broken up and dissipated before they pass into the firing chamber, and the movement of gases through the kiln is slow, even, and "blast-free."

(5) Because of the large number of individually small radial flames in each burner and because the entire combustion reaction (even at high rates) occurs wholly within the cup concavity, large turndown ratios of 40 to 1 or even 50 to 1 are practical, and individual burner adjustments or the responses of burners to automatic control are faster and more effective.

The significance of these five basic attributes of the Selas radiant-cup gas burner will become apparent as application techniques are discussed.

Figure 2 (intentionally underexposed) shows at the left an actual burner in operation with a conventional torch-type burner utilizing the same amount of the same coke-oven gas premixed with the same quantity of air. The incandescence is uniform over the ceramic cup, and there is a total absence of flame beyond the burner face in contrast to the variable incandescence of the burner at the right and the "torching" of the flame beyond the burner face.

Figure 3 is a cross section of the model Selas radiant gas burner utilized in production kilns using direct radiant gas firing. This design represents the latest improvements, namely, (1) the flexible connection between the burner and the inlet piping to allow for expansion and contraction by heating and cooling, (2) the all-ceramic construction (no metal is used between the inside face of the kiln wall and the kiln shell), (3) the variety* of ceramic compositions matched to service conditions in the various parts of the assembly, (4) the "expander" elements which allow for adjustment to any wall thickness, and (5) the give-and-take, spring-

* See p. 134 for star footnote.

loaded positioning of the tip and tip holder. The single-pipe fuel supply, moreover, makes manifolding simple.

III. Case Histories

(1) Recently Developed Application Technique

Since the first full-scale demonstration of direct radiant gas firing in fine china-bisque production,[1] seven companies in the ceramic industry have installed thirteen kilns involving approximately 700 refractory-cup burners (Fig. 3). More than one third, or five of the thirteen kilns, are large circular continuous units, four are straight types, and four are periodics. The ware processed in ten of these units is highest quality china-bisque, microporous porcelains, intricate high-temperature refractory shapes, or steatite mechanical and electrical porcelain bodies; in two, only glostware is fired; and in one, the ware is single-fired (bisque and glost). Ten of the kilns are used for the main production; three, for specialty or experimental work involving "limit" or "beyond-normal" conditions relating to temperature-time cycles or kiln atmospheres; four were of original design and build; three were older kilns converted to modern direct radiant gas firing from oil or crudely applied gas; and six were designed and built by well-known kiln builders.

Experience in the design, construction, and operation of these kilns has given valuable information on radiant burner application technique.

(1) As the name of the firing method implies, no muffles, baffles, or fire tubes need be employed because (*a*) all combustion is completed within the burner long before kiln gases touch the ware; (*b*) a uniformly blastfree controllable flow of kiln gases can be arranged, and (*c*) exceptional heating uniformity can be accomplished without intermediate heat retarders or distributors. Resultant advantages include higher heating efficiencies and more immediate response of working zone temperatures to adjustment (manual or automatic) or, in terms of heat balance, the elimination of the high-heat storage capacities and the time of heat conduction through muffles or fire-tube materials.

The "flywheel" effect of the kiln walls and arch can also be greatly reduced over conventional methods (wherein the kiln walls themselves are the major source of heat, and the gas input cannot be changed suddenly and still give an immediate decrease or increase in kiln temperature). Even if walls are made of the best insulating refractories, this heat inertia or flywheel effect cannot be avoided in conventionally fired kilns or furnaces. Where radiant-cup burners are used, however, the burners rather than the kiln walls become the predominant heat source, and burner input adjust-

* As many as five compositions in some burner designs; for example, the intricate flame distribution tip must stand up indefinitely under a 2000°F. temperature differential along its $1^1/_2$-in. length; the cup must be rough of surface and retain contour without spalling under protracted incandescence and rather violent heat shock; parts around the tip holder should be highly insulating; the burner block itself must be refractory and reasonably immune to cracking; and the ring against which the tip holder seats must be wear resistant to maintain perfect spacial relationship between port slots and incandescent cup.

FIG. 4.—Inside view of high-heat zone of Lenox kiln during construction.

FIG. 5.—Straight kiln converted from oil; used for single firing mechanical and novelty ware at 2200° to 2400°F.

FIG. 6.—Outside view of arrangement of multiple radiant burners in circular kiln wall.

FIG. 7.—Converted straight kiln with different type of rigid burner connection.

ments (affecting the "temperature head" between the cup surface and ware) are immediately reflected in ware heating rates.

(2) The second application technique is the use of many burners in predetermined patterns to establish cross-kiln and car-to-arch temperature uniformity. Figure 4 shows the inside of the high-heat zone of a kiln during construction. Twenty-one radiant-cup burners are visible, and their staggered placement (with more at hearth level than at higher levels) assures absolute temperature uniformity throughout the charge. Actual temperature measurements across the charge (30 in.) and from bottom to top piece (36 in.) at all stations (determined by pyrometric cones as well as by thermocouples) showed no detectable differences (less than 3°F.). Figure 5 shows a straight type of kiln converted from oil and used for the single firing at 2200° to 2400°F. of five to seven tons per day of mechanical and novelty ware as well as for biscuit and for glaze alone. Two rows of radiant burners are employed, and temperature uniformities throughout the charge on any car are within ±5°F. Previously, with full-muffle oil firing, 108°F. differences between top and bottom pieces were not unusual. The use of hard-faced tile to eliminate "dusting" on glazes may be seen in this figure.

Figure 6 shows an outside view of the multiple radiant burners in the wall of a circular kiln. These burners do not possess the more recent built-in, flexible ceramic-to-metal joints and therefore require connections to the manifold lines by flexible tubing. In the kilns constructed more recently, less expensive, neater, and simpler rigid connections are practical.

(3) Figure 6 also shows the combustion control equipment and is a clue to a third point of correct radiant burner application. Gas flows in through the vertical pipe (left of center) and is conducted through a zero governor to an automatic mixing valve. On the other side of the mixing valve is the large filter through which air is drawn. The mixing valve is of the sleeve type with precisely machined ports so that (irrespective of demand or gas-line pressure or air-pressure variations beyond the inlet filter) the proper ratio of gas and air to be premixed can be adjusted and thereafter automatically maintained. The delivery turbo-type blower draws the premixed fuel from the mixing valve and delivers it through the blowoff relief and the various fire checks to the burner system at constant pressure. Close and consistent control of temperature and kiln atmosphere is maintained by using the finest type of positive-pressure machine premixing of fuel and air.

(4) Figure 7 shows a converted straight kiln (with a different type of rigid burner connection) which regulates time-temperature cycles along the length of travel through the kiln by the longitudinal spacing of burners. Two zones of control in the high-temperature section of the kiln are visible. The adjustments, spacing, and sizing of burners in one zone regulate the rate at which the ware is brought up to maturing temperatures; and the same factors in the second zone govern the uniformity of temperature along the length of the "maturing" or "soaking" part of the cycle.

FIG. 8.—Open setters in direct radiant gas firing as substitute for saggers.

FIG. 9.—Small straight continuous kiln converted to direct radiant gas firing.

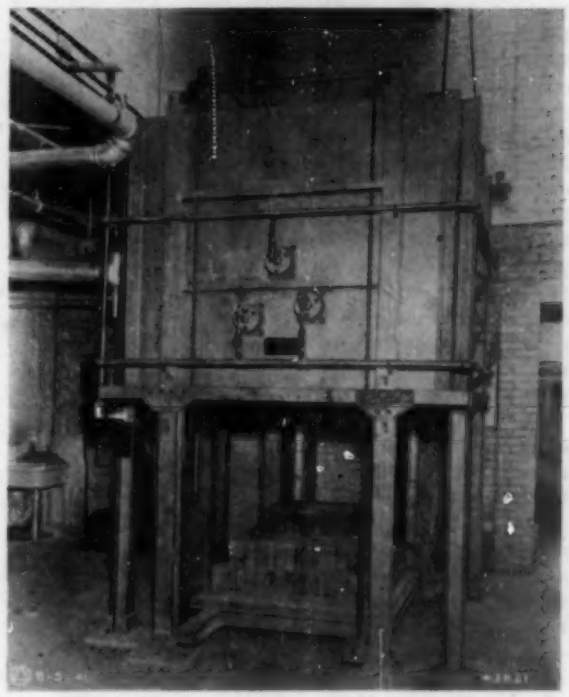

FIG. 10.—Elevator hearth construction and complete sealing of firing chamber.

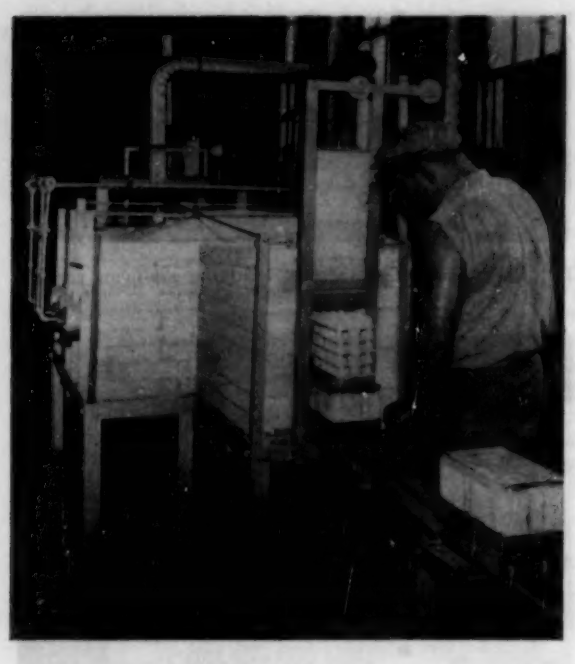

FIG. 11.—Continuous midget straight kiln with controlled preheat, firing, and cooling zones.

(5) Figure 8 suggests an application technique often made possible by direct radiant gas firing, that is, the elimination of saggers. A sagger, in effect, is another protective muffle, and radiant firing eliminates the necessity of muffles to protect the ware from the variable compositions and "torching" of incompletely combusted gases which characterize most conventional firing methods. Open setters are shown, as developed by Leslie Brown of Lenox, Incorporated. Most of the ware fired in the installations being discussed is arranged in open stacks, despite the fact that it may be first-grade china, fine glost, closest-tolerance steatite, or precision high-temperature burner parts. With the elimination of muffle refractories or fire-tube materials, much of the kiln furniture and even loose flint and saggers, desired temperature conditions may be established within the ware in a minimum of time, and the length of soaking periods may be reduced with direct radiant gas firing.

(6) A final and new application technique with direct radiant gas firing is the establishment of different atmosphere conditions in different zones of the same furnace. In four circular kilns recently placed in operation, one region of each kiln is operated with one atmosphere, whereas other regions are operated with another atmosphere (conceivably one zone could be reducing while another zone is oxidizing). There are, moreover, no muffles or baffles between burners and ware, or between the various furnace atmosphere zones. Fuel-air supplies of different premixture ratios must, of course, be supplied to those zones where different combustion product compositions are maintained.

IV. Miscellaneous Kiln Applications

Figure 9 shows a relatively small straight continuous kiln converted to direct radiant gas firing for a variety of close-tolerance mechanical forms, chemical porcelain, and refractory parts. The hot kiln gases and cooling air can be manipulated with as much facility as in muffle kilns. The preheat section is heated entirely by combustion products drawn from the direct-fired firing chamber, the gases being kept near hearth level by the tile or baffles located there. The advantages of direct-radiant firing in the high-heat zone are a saving of fuel, temperature control, quick kiln response, production speed, and shortened cycles, even though the preheat chamber is baffled to avoid hot gas stratification. There are other proprietary methods to avoid this stratification which involve no baffles at all. In a larger, higher-production installation, the products of combustion could be recirculated in the preheat zone for maximum thermal efficiency.

The kiln shown in Fig. 10 is interesting because of its elevator hearth construction and the complete sealing of the firing chamber. In addition to the sand seal, there is also a step in the plug-type hearth which may be grouted if desired. Three of these periodic kilns are in use for firing to 2650°F. and under special atmosphere conditions which are not common to large-volume continuous production. One such kiln is used by this Company in the manufacture of close-tolerance burner parts (such as radiant burner tips), and Lenox uses the same type of kiln for unusual glazes, experimental work, and fritting. As will be observed, three burners staggered in each of the four sides are employed. The chargeable space is about 2 cu. ft. This type of periodic kiln is useful for rapid cooling because the elevator hearth may be lowered sufficiently to allow enough infiltration of air to cool at the desired rate.

The continuous midget kiln in Fig. 11 is interesting because, despite its size, cycles are completely engineered and fully controllable in all three zones, the preheat, firing, and cooling. The cars carry a stack only 6 in. wide by 6 in. high and ride on roller-skate wheels. Of the six direct radiant burners (three on a side), one is used for preheat and two for high-temperature firing. This installation is used for "pilot" operations to establish cycles and mixes and also for plant control. Certain glazes have been satisfactorily fired in this kiln on cycles as short as three hours.

Direct radiant gas firing is being used in New England to produce a special, extra-hard abrasion-resistant ceramic material to replace tungsten carbide in sand-blast nozzles and thread guides for high-speed textile machinery.

V. Other Uses

In fire polishing glass products, in forehearths and feeder baths of glassmelting tanks, and in baking fluorescent coatings on the inside of lamp tubing, the use of radiant gas burners has become the means of improved processing. Radiant gas combustion in drying plaster molds for slip casting is also being studied.

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